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HERBICIDE CONTAMINATION OF SURFACE RUNOFF WATERS

John O. Evans, et al

Utah State University

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Herbicide Contamination of Surface Runoff Waters

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HERBICIDE CONTAMINATION OF SURFACE RUNOFF WATERS

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ABSTRACT

Field and laboratory studies of the movement of herbicides were conducted to determine their potential as contaminants in irrigation return flow. Special emphasis was given to the use of herbicides for vegetation control along ditches, canals and watersheds where high dosages are required to control the excessive growth of grasses and broad-leaved weeds. The following herbicides have been studied: substituted urea (diuron), triazines (summitol and atrazine), phenoxyacetic acid (2, 4-D and 2, 4, 5-T) and a substituted pyridine (picloram).

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SECTION I

CONCLUSIONS

1. Many studies have been made to determine the levels of herbicides in irrigation water and to determine the effects of herbicide residues in water. The low concentrations that are observed following proper application of the herbicides would not likely be hazardous to crops or animals.

2. Herbicides can be detected in ditch and canal water subsequent to treating the bank to control vegetation. The herbicides are rapidly diluted and within a short distance are not detectable by using plants or gas-liquid chromatography.

3. Soil properties play a major role in determining the movement of herbicides in water. Organic matter content, pH, cation exchange capacity and sesquioxides are the most important soil properties influencing the adsorption or release of herbicides. Soil type plays a minor role in this regard. Five soils were compared for their tendency to adsorb and release the herbicide, picloram. The adsorption of the herbicide from water containing 1.0 ppm picloram ranged from 11 to 52% among the five soils.

4. The release of herbicides from soil into surface waters was primarily regulated by organic matter, pH and cation exchange capacities of soils. Fifty percent of the adsorbed picloram was eluted with four flushings of water. Continuous flushing with water resulted in the complete removal of picloram within 24 hours for all soils studied.

5. Concentrations of herbicides in surface water were reduced probably by infiltration of a portion of the contaminated water into the soil and by dilution with additional water. Under field conditions, this reduction occurred within a few hundred meters distance below the treated areas.

6. The adsorption and release of picloram by soils is influenced by the salt load of the soil. Calcium saturation of a highly adsorptive soil further increased its capacity to adsorb the herbicide. The enhanced picloram adsorption could not be accounted for by the increase in undissociated picloram as a result of the drop in pH caused by salt additions. Further tests demonstrated that picloram did not precipitate from solution in the presence of the salts as is commonly observed among other organic molecules.

SECTION II

RECOMMENDATIONS

The study was quite exhaustive with regard to the movement of picloram in soil and water but other herbicides were limited to one or two field trials and consequently cannot be considered in detail. The recommendations will pertain primarily to picloram and its effects on the quality of irrigation return flow.

Under field conditions, picloram does not present a serious threat to water quality a short distance downstream from the site of application. It is evident that precautions given on the herbicide label are adequate to allow the material to be used safely. To avoid crop or other plant injury, do not treat or allow picloram to fall directly into water and do not treat bottoms of irrigation ditches. Broadleaved plants such as potato, bean, cucumber, alfalfa and others are very sensitive to picloram and should not be irrigated with water from picloram treated areas a short distance from the crops.

A very small fraction of the applied herbicide tends to move into water coming into contact with a treated soil surface. The quantity that moves with the surface water decreases rapidly as rainfall or irrigation moves the herbicide into the soil where it is strongly adsorbed onto the soil colloids and subsequently broken down by chemical and biological processes. Once adsorbed onto soils, picloram is slowly released with continuous flushing with water. The flushing tends to reduce its concentration to levels which are nontoxic to plants. The total quantity of picloram adsorbed on the five soils studied was recovered with a 24 hour period of continuous flushing. Soil particles that are eroded with excessive surface water may carry significant amounts of the herbicide. Care should be taken to minimize soil erosion in treated areas. Excessive dosages of picloram tend to denude the soil and therefore hasten soil erosion. Further studies are needed to ascertain the desorption characteristics of herbicides sorbed on soil particles and hence the effect of suspended soil on the concentrations of herbicides in water.

Picloram might be removed from water by diverting the contaminated water to holding areas where it will come into contact with soil or other adsorbant materials. Water contaminated with picloram adsorbed on suspended material could be decontaminated by this procedure if the suspended particles will settle out upon standing.

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SECTION III

INTRODUCTION

Since runoff from agricultural and watershed lands and other areas treated with pesticides may offer a potential hazard to the health of both animal and plant life, there has been a growing concern over possible contamination of water systems by runoff from these areas. The continued use of presently registered herbicides and new candidate herbicides may depend on our ability to answer questions as to their movement in soil and water, effects on other crops, and other environmental effects.

Considerable information exists concerning many of the common inorganic constituents in surface waters and streams. Much less is known about the herbicidal composition of surface runoff waters or irrigation return flow from treated lands and, further, the existing data are seldom associated with known properties of a watershed. The demonstrated presence of herbicides in some streams indicates their movement from treated sites to nontarget areas where their effects may constitute a hazard. Each use of water affects its quality and hence its performance for downstream users. The demand for high quality water coupled with the ever-increasing use of all types of agricultural chemicals has completely changed public attitudes toward the region's water resources. Under multiple use, each user has an obligation to maintain quality at the highest practicable level. Little is known of the effects of various pest control practices on the quality of water and hence on its suitability for municipal, industrial, recreational, or other uses.

Herbicides can enter surface waters in any of three ways: (a) direct application to water, (b) via surface runoff, including erosion of surface soils from treated areas, and (c) via movement through the soil to ground water that later drains into surface streams. If movement in surface runoff is demonstrated to be a significant source of pollution, then control is more difficult and it may have to come by restricting the use of some chemicals. Few data are available on the movement of pesticides or their metabolic products in runoff waters or through the plant root zone.

In the western states, agriculture has long been concerned with the consequences of water quality for soil conservation and crop production. Maintenance of a permanent irrigated agriculture depends upon

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an understanding of the interactions of soil, water and vegetation. An important part of this success is the judicious use of agricultural chemicals as fertilizers, amendments and for pest control. The effects of these chemicals on water quality has, however, received little attention because this aspect has little apparent relation to crop production and its importance to nonagricultural users of water was not appreciated. Since most water entering the public water supply drains from forest, range or farm land, the downstream user quite naturally attributes undesirable quality of water to its management on land within the watershed.

Conflicts of concept and interest are likely to arise between those concerned with public health, wildlife, or recreation and those concerned with timber and food production unless each group understands fully the consequences of each use of the available water. For these reasons agriculture must come to appreciate how its management of soil and water resources may affect the quality of water for nonagricultural users.

A research program concerned with the impact of agriculture on the quality of water is particularly appropriate for the western region because irrigation plays a major role in crop production and irrigation return flows often constitute a major share of the waters that enter municipal or industrial water supplies or that support fisheries or recreation. This project is concerned primarily with the movement of agricultural chemicals from treated areas by surface waters coming in contact with the soil or movement through the soil profile by leaching.

Objectives

The purpose of this investigation was an objective study of the interactions between agricultural chemicals, soils, and water that may result in the degradation or pollution of surface and ground waters.

Specifically the objectives were:

1. To study, under field conditions, the potential movement of herbicides from treated sites via surface runoff water and movement through the soil.
2. To determine the physical and chemical properties of some herbicides and soils that are associated with herbicide movement.

3. To develop analytical techniques for some herbicides to detect the submicrogram quantities that are involved.

Organization of Research

Field Studies

The major objective was to determine the contamination of water by surface flow in the field through the use of small watershed or erosion-runoff study areas where the amount and quality of runoff could be determined. Closed or well defined drainage areas were used to better identify the materials added or removed from the system.

Two sites with different soil characteristics were selected where surface runoff could be measured. Herbicides of known adsorption characteristics were surface applied; soil and water samples were taken throughout a two year interval to demonstrate the presence or absence of the herbicides in the samples. The approach was to select areas of known drainage characteristics and establish plots that were treated differentially to determine the role of rate and time of herbicide application and quantity and intensity of subsequent precipitation on the movement of selected herbicides.

Laboratory Studies

Leaching columns of varying lengths were used to follow adsorption, release and movement of selected herbicides applied to soils of differing texture, organic matter content, calcium carbonate content, and exchangeable cation status. An attempt was made to account for all applied materials by analysis of leachates and column sections. Radiotracer techniques were used, when applicable, to follow movement of tagged materials. The herbicides were applied at normal field rates and at multiples thereof. Movement was followed under conditions of continuous leaching, and also by applying the leaching solution in increments and allowing sufficient time for equilibration between applications. Extent of exchange between soil and water was related to both physical and chemical properties of the herbicides and soils.

Equilibrium studies were conducted to relate the chemical nature of picloram (4-amino-3, 5, 6-trichloropicolinic acid), soil texture and

inorganic salts to adsorption and desorption. The effect of pH, temperature, base saturation and drying on desorption, movement and degradation was studied. This report is organized according to the two major areas of investigation; field studies and laboratory investigations.

SECTION IV

LITERATURE REVIEW

Field Studies

Growing concern has been expressed lately by scientists and others over the possible contamination of water systems from the runoff of agricultural and watershed areas (47, 61). Mullison (47) stated that drainage from watersheds and other herbicide treated areas offer a potential hazard by possibly causing harmful effects to the health of domestic animals, wildlife, aquatic invertebrates and vertebrates as well as man. A publication (5) of the National Academy of Sciences indicated that herbicides may be carried from their point of application to unsprayed areas in surface-water drainage. It also pointed out that when excess rainfall or irrigation water drains from fields, herbicide molecules may be carried in solution or in the adsorbed phase on suspended soil particles and become deposited along the path of the flowing water. Allan (3) stated that herbicides are not known to be accumulated by plankton or aquatic fauna and that water pollution by runoff from treated land is not presently a problem. However, existing and new herbicides must be examined periodically with the express purpose of preventing environmental contamination. White et al. (61) conducted a study on the losses of atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) from fallow land caused by runoff and erosion. In their study, atrazine was applied to the surface of a fallow field at 3 lb/A and simulated rainfall was used to produce runoff. A simulated rainfall of 2.5 inches in 1 hour applied 96 hours after the herbicide application, caused 7.3% or 0.24 lb/A of the atrazine to be lost. They mentioned that a storm of this intensity comes only about once in 10 years and that the losses from this type of storm would be considerably greater than the normal storm encountered in the area. They reported that a common size storm (0.5 inch) for the area simulated 96 hours after herbicide application resulted in 0.06 lb/A or only 25% as much herbicide loss as the 2.5 inch simulated rainfall. It was stated that the concentration of atrazine in the soil fraction of the runoff was higher than in the water fraction but that most of the atrazine transported was associated with the water fraction due to the larger amounts of water lost as compared with soil. Their study also showed that the average concentration of atrazine in the runoff decreased with increase in storm size.

Mullison (47) reports: "There is little evidence that herbicides from agronomic or industrial usage are reaching or accumulating in our water supplies in amounts to cause a pollution problem."

The Senate Select Committee on Water Resources has stated that "water pollution from agricultural chemicals is not as extensive as some would lead us to believe" (57).

Many studies have been made to determine the effects of herbicidal residues in water. The low concentrations that are observed following application of herbicides would not likely be hazardous to crops or animals.

In spite of the many benefits from agricultural chemical usage, any biologically active chemical implies a potential hazard that should be evaluated. In general, herbicides are of a relatively low order of toxicity and the potential for these being a source of pollution is minimized.

There is a potential hazard dealing with ditchbank weed control if herbicide applications are followed by heavy, intense rainfall, whereby large amounts of herbicide may be washed into the channel.

Recent research has emphasized the dissipation of picloram from impounded water (56) and from runoff water and soils (52). Soil texture, application rate, season of application, and time interval after treatment were important in the dissipation of picloram from pasture soils in Nebraska (52). The time interval from application to the first irrigation affected the amount of picloram removed with surface runoff or leached into the soil profile of semi-arid rangelands (53). Movement studies indicated that leaching was an important means of dissipating the herbicide in light textured soils. Surface movement of picloram from sod-covered and fallow plots occurs with irrigation sufficient to cause runoff (56). In the studies by Trichell et al. (56), approximately 5% of the picloram was lost in runoff water when 1.25 cm of simulated rainfall was applied in 1 hour at 24 hours after herbicide treatment. Picloram was readily degraded in clear water by ultraviolet light. However, degradation from a soil surface by sunlight was considerably slower than when the herbicide was in aqueous solution. No definitive information was available as to the occurrence and persistence of picloram in natural water sources following application to the grassland ecosystem.

Laboratory Studies

Laboratory investigations reported in the literature on the adsorption-desorption and movement of picloram in soils are similar to work done on the triazines and other herbicides. Also, since picloram is an anion at the pH range of this study, some literature has been included on the interactions in soil of inorganic anions like phosphates, borates and sulfates.

Adsorption-Desorption of Pesticides in General

Factors Affecting Adsorption-Desorption

s-Triazine Herbicides. The structure of atrazine, a common member of this family, is shown in Appendix A. The pKa ($pKa = -\log_{10} Ka$, Ka is the thermodynamic dissociation constant) of this compound is about 1.68 and solubility in water is about 70 ppm at 27° C (6). It should, then, behave as a molecular species at pH above ≈ 3.68 (pKa + 2).

Harris and Warren (28) reported atrazine to be adsorbed by both anion and cation exchangers, to be slightly adsorbed by muck soil, and to be greatly adsorbed by bentonite. Desorption occurred more readily from bentonite than from muck. Talbert and Fletchall (55) found montmorillonite to be very adsorptive of atrazine, while no herbicide was adsorbed on kaolinite. Organic materials were more adsorptive than clays.

Hilton and Yuen (31) found atrazine to be quite readily adsorbed on several Hawaiian soils but could not correlate adsorption with any soil property. Harris (27) found atrazine to be adsorbed in greater quantities by fine textured soils than by coarse textured soils.

To further understand the behavior of atrazine, a nitrogen containing ring compound, in soils, the effect of pH and temperature on its adsorption-desorption was examined by Harris and Warren (28). They found that atrazine adsorption on muck was temperature independent, while adsorption on bentonite was temperature dependent. Talbert and Fletchall (55) reported that increases in temperature decreased atrazine adsorption on montmorillonite and organic materials.

McGlamery and Slife (40) reported very slight changes in adsorption of atrazine by a Drummer clay loam soil with temperatures in the range of 0.5° C to 40.0° C. Desorption was increased by increases in temperature in the same range. However, adsorption of atrazine by humic acid was found by these authors to increase with increases in temperature. Desorption from humic acid was very slight. These workers proposed van der Waal's forces as the bonding mechanism in adsorption on clays and ionic bonding in humic acid.

Concerning the effect of pH, Talbert and Fletchall (55) reported that adsorption of atrazine by montmorillonite and organic materials was decreased by an increase in pH in the range of 5.0 to 7.0. McGlamery and Slife (40) found similar results in the pH range of 3.9 to 8.0, for atrazine adsorption on Drummer clay loam soil and humic acid. Desorption of atrazine from the same soil was increased by increases in pH. Desorption from humic acid was very slight.

Another compound, of the s-triazine family, prometone, has a pKa of 4.30. Prometone exists in molecular form in a neutral aqueous environment and associates strongly with hydrogen as the pH is lowered. Weber, Perry, and Upchurch (59) found that prometone was not adsorbed by kaolinite, but gave s-shaped curves on sodium and/or aluminum montmorillonite, and the adsorption was inversely related to pH and temperature.

Phenyl Alkanoic Acid Herbicides. The general molecular structure of this family of compounds appears in Appendix A.

Weber, Perry and Upchurch (59) found the 2,4-D (pKa = 2.80) was negatively adsorbed by clay minerals. Frissel and Bolt (18) also obtained similar results. However, Haque et al. (29) found positive adsorption of 2,4-D on the clay minerals illite, kaolinite, and montmorillonite, although adsorption on kaolinite was minimal. Temperature had little effect on the amount adsorbed.

Bailey, White, and Rothberg (7), studying the effect of pH on 2,4-D and 2,4,5-T (pKa = 3.14) adsorption by montmorillonite, found that the magnitude of adsorption of these compounds was governed by the surface acidity and not by the pH of suspension.

Effect of Inorganic Salts on
Adsorption-Desorption of Pesticides

The paper of Frissel and Bolt (18) was the earliest report found concerning the effect of inorganic salts on pesticide adsorption. These authors, working with clay minerals, found that the main variables in the adsorption of a number of organic acidic and basic herbicides, were pH and electrolyte concentration of the system. They explained the salt effect on the basis of "salting out".

Nearpass (49) studied the effects of the predominating cation (Ca, Mg, K, & Na) on the adsorption of simazine ($pK_1 = 1.65$, $pK_2 = 0$) and atrazine (pKa = 1.68) by Bayboro clay soil. He found that adsorption of these herbicides decreased with increasing degree of saturation with these cations. The decrease appeared to be a result of the occupation of adsorption sites by metal cations, rather than a specific effect of cation species on the adsorption of the herbicide. He also studied the exchange adsorption of amitrole (3-amino-1, 2, 4-triazole, pKa = 4.14) by montmorillonite, including the effect of $CaCl_2$ and NaCl on amitrole's adsorption (50). A decrease in amitrole adsorption was observed with an increase in salt concentration, which he attributed to occupation of adsorption sites with metal cations. He concluded that adsorption of amitrole by neutral or alkaline soils may be due to molecular adsorption by organic matter.

The importance of exchange type reactions in the adsorption-desorption of charged herbicides is indicated by the work of Weber and Weed (60). They found that diquat and paraquat (completely ionized) cations were adsorbed by montmorillonitic and kaolinitic clay minerals to the extent of their cation exchange capacity. About 80 percent of each of the herbicides was displaced from kaolinitic clay with Ba^{+2} ions, whereas only 5 percent was removed from montmorillonite. The nerbicides were found to exchange for one another. Prometone, a neutral herbicide, was adsorbed by montmorillonite but only slightly by kaolinite. It was released from both minerals more readily with deionized water than with Ba^{+2} ions (1M $BaCl_2$).

MacNamara and Toth (38) studied the effect of weak electrolyte solutions on the adsorption of linuron and malathion by soils and clay minerals and found that, in general, electrolytes suppressed adsorption under some conditions but had no effect under most conditions

and did not increase the desorption of either linuron or malathion from soils.

Hance (26) investigated the effect of exchangeable cations on the adsorption of linuron and atrazine by a cation-exchange resin, cellulose phosphate powder, bentonite, and a peat soil. The cations studied were Ca^{+2}, Ni^{+2}, Cu^{+2}, Fe^{+3}, and Ce^{+4}. The results with linuron are consistent with the hypothesis that complex formation with exchangeable cations is a possible mechanism of adsorption. This was not true with atrazine.

Abernathy and Davidson (1) studied the effect of $CaCl_2$, at 0.01 and 0.5N concentrations, on the adsorption of prometryne (pKa = 3.05) and fluometuron (a neutral species) in soil. In batch equilibrium studies, fluometuron adsorption was decreased and prometryne adsorption increased by increasing the $CaCl_2$ concentration from 0.01 to 0.5N. The mobility of prometryne decreased in the two soils by increasing the $CaCl_2$ concentration. Fluometuron mobility was unchanged by the two $CaCl_2$ concentrations in one soil, but increased in another soil (Norge loam) at the high $CaCl_2$ concentration.

Effects of Inorganic Salts on the
Adsorption of Inorganic Anions

Hadas and Hagin (23) studied boron adsorption by soils as influenced by potassium (K). Potassium-saturated soils adsorbed more boron than the untreated soils, and Langmuir equations indicated a greater strength of adsorption by the K-treated soils. They concluded that potassium influenced the adsorption of boron probably by creating more favorable conditions for boron adsorption in soil.

Barrow (8) studied the influence of solution concentration of Ca^{+2} on the adsorption of phosphate, sulfate, and molybdate by soils. He showed that adsorption of all three anions increased as the Ca concentration in soil increased. It was shown that simultaneous increase in exchangeable Ca also occurred.

Movement in Columns and Application of Chromatographic Theory

Elrick, Erh, and Krupp (16) devised an apparatus to study miscible displacement processes in soils. The usefulness of this technique was illustrated by a brief description of (a) the mixing of Cl^- in a glass bead medium; (b) the movement and adsorption of atrazine in soil; and (c) the movement and microbiological nitrification of NH_4^+-N to NO_3^--N. Non-conformity of the mathematical model to the actual movement of atrazine in soil columns was attributed to intra-aggregate adsorption and dead-end pores.

Lindstrom et al. (37) developed an equation based on chromatographic theory to predict the theoretical curves for pesticide movement for two different boundary conditions in saturated soil for various pore water velocities and diffusion coefficients. They did not test their model experimentally.

Using miscible displacement techniques to move solutions containing fluometuron (a neutral species) and diuron (pKa = 1 to 2) through saturated beds of 250-μ glass beads and through Norge loam soil columns at two water flow rates, Davidson and Santelmann (14), found that (a) more diuron than fluometuron was absorbed by the glass bead system, (b) the shape of fluometuron distribution curves at two flow rates were distinctly different, and (c) fluometuron was as mobile as the chloride ion at both high and low flow rates.

Davidson, Rieck, and Santelmann (13) found that the rate at which fluometuron and diuron (two substituted urea herbicides) move through a water saturated glass bead column and uniformly packed soil column depends upon water flux. Experimental and calculated effluent concentration distribution (based on a model similar to the one used in this study) did not agree when fluometuron was adsorbed by the porous material (soil).

Davidson and Chang (12) applied the chromatographic theory of pesticide movement to picloram movement in soils. They demonstrated that average pore water velocity influenced picloram movement more significantly than variations in bulk density or largest aggregate size at a given flow rate. The model based on chromatographic theory failed to predict picloram movement, which they attributed to

complexities of the adsorption process including the influence of pore size distribution.

King and McCarty (34) employed an equation describing the chromatographic movement of pesticides under noncontinuous flow conditions. Experimental and theoretical curves agreed fairly well for the leaching of organic phosphorus insecticides in soil columns.

Adsorption-Desorption of Picloram

Factors Affecting Adsorption-Desorption

Soils. Grover (21) investigated the relationship between the amount of picloram needed to reduce fresh weight of sunflowers by 50 percent (ED_{50}) and clay content, organic matter, and cation exchange capacity of seven Saskatchewan soils maintained under controlled environmental conditions. There vere no significant correlations between ED_{50} values of picloram and soil clay content or cation exchange capacity. ED_{50} values were highly correlated with soil organic matter content, and increased as the soil pH was lowered or raised from pH 6.5.

Hamaker, Goring, and Youngson (24) found the greatest adsorption of picloram, 2,4-D and 2,4,5-T in soils containing a high percentage of organic matter, in soils rich in Fe and Al components (red soils) and in acidic soils. Adsorption occurred rapidly by red soils but slowly by highly organic soils. The data suggest that adsorption of picloram is primarily caused by organic matter and hydrated metal oxides, with clays probably playing a minor role. Adsorption of nonionized picloram and its anion was involved.

Herr, Stroube, and Ray (30) and Keys and Friesen (36) found that resistance to leaching of picloram in soils was correlated with adsorption. Herr, Stroube, and Ray (30) also observed that picloram adsorption in soils was inversely related to pH and directly related to organic matter of the soil.

Exchange Resins, Clay Minerals and Other Adsorptive Materials. Bailey, White, and Rothberg (7) reported conformity to Freundlich adsorption equation for picloram, when its aqueous solution was

incubated with samples of 1 to 0.2 μ (micron) montmorillonite clays adjusted to pH values of 3.35 and 6.80. They concluded that adsorption occurred to the greatest extent on the acid H-montmorillonite compared to the nearly neutral Na-montmorillonite. Negative adsorption occurred when the adsorbent was Na-montmorillonite. There appeared to be slightly more of a driving force (molar free energy) for adsorption of picloram than for phenoxyacetic acid, although the difference in average free energy ($\overline{F}$) values for the hydrogen system was not great.

Grover (21) studied the adsorption of picloram by various soils, activated charcoal, anion and cation exchange resin, kaolinite and montmorillonite, wheat straw, cellulose powder, cellulose triacetate, and peat moss. He concluded that adsorption of the molecular form probably would involve hydrogen bonding with hydrophobic surfaces, e.g. those on cellulose triacetate and peat moss. The absence of adsorption on clay minerals and cellulose powder suggested a total lack of attraction of both forms of picloram for hydrophilic surfaces.

Field Studies and Movement in Different Media

Herr, Stroube, and Ray (30) found that the region of highest concentration of picloram in heavy and medium-textured soils, when sampled 9 and 15 months after application, was near the surface.

Merkle, Bovey, and Davis (43) investigated the effect of soil type, temperature, and moisture on the persistence of picloram. Detectable quantities of picloram were present in Houston clay, Axtell sandy loam, and commercial sand after incubation for one year, at 4, 20, 38° C and moisture levels of both field capacity and 0.1 field capacity, from rates as low as 0.25 μg per gram soil (0.5 lb/A). Movement studies indicated that leaching was an important means of dissipating the herbicide in light soils; picloram moved completely through the surface 2 feet of soil; the greatest herbicide concentrations generally were found at the deepest sampling depth.

SECTION V

MATERIALS AND METHODS

The herbicides diuron (substituted urea); atrazine and GS-14254 (s-triazines); 2,4-D, 2,4,5-T and picloram (plant hormone types) have been evaluated for their tendency to move from treated lands in surface flowing water and a more thorough study was made to determine whether picloram might also be desorbed from soils to move in ground water percolating through the soil and ultimately be discharged into streams nearby.

Field Studies

Several experiments were conducted over a 3-year period to evaluate the amount of movement of several herbicides when they were employed as currently recommended for vegetation control along irrigation canals and watershed areas.

Movement of Herbicides Following Heavy Dosage Applications to Irrigation Canal Banks

An irrigation canal in Trenton, Utah with a 60-70 cfs maximum discharge was selected as a test site since it was infested with several troublesome plant species and represented many similar canals in the state. During the 1968 irrigation season, four plots along the canal were selected and staked; the treatments were made with a 6-foot boom sprayer on November 4 after the water was removed from the canal. Two plots were treated with diuron at 30 lb/A and the remaining two plots down the canal were treated with 10 lb/A atrazine. Each plot was 500 feet long and extended from 5 feet above the water line on the bank to the bottom of the canal; both banks were treated making the plots approximately 20 feet wide. The four plots were spaced approximately one-half mile apart along the canal. Water samples were taken in May, 1969 as the canal received the first water. One liter samples were taken of the first flush of water and a second collection was made when the canal reached approximately 90 percent of its capacity 4 hours later. Duplicate samples were taken 10, 100 and 1000 feet downstream from each plot.

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A similar test was conducted on the North Logan-Smithfield canal near Logan, Utah. Two 20 by 500 foot plots were treated with 30 lb/A diuron on December 2, 1968 and two plots received 10 lb/A atrazine the same day. Plots were approximately one-half mile apart to facilitate sampling at 10, 100 and 1000 foot distances below the plots. Duplicate one-liter samples were taken when the first flush of irrigation water reached the treated areas and again the same day when the canal was approximately 60 percent of its 80 cfs maximum discharge. The water samples were taken to the laboratory and prepared for analysis within three hours after collection.

Diuron Analysis

The water samples were analyzed chromatographically for herbicide residues using the experimental procedure of McKone and Hance (42).

One hundred ml of water was measured into a 250 ml separatory funnel and extracted for 1 minute each with two 25 ml portions of dichloromethane. The organic layers were collected in a separate 250 ml separatory funnel. The solution was concentrated to about .5 ml under reduced pressure on a water bath at 35° C. The remaining solvent was removed with a stream of air. Five ml of saturated sodium chloride solution was added and the flask was shaken for 15 seconds. Fifteen ml of 2, 2, 4-trimethylpentane was added and the flask shaken for 1 minute. Aliquots of the upper 2, 2, 4-trimethylpentane layer were taken and diluted for gas chromatography.

A Hewlett Packard 5750 gas chromatograph was used with a 1.8 m by 3 mm i.d. glass column packed with 3.5% DC 200 on 80 - 100 mesh Gas Chrom. The injector temperature was 200° C, the detector 225° C, and the column 150° C.

A standard solution of diuron containing 1 mg/ml was prepared in redistilled methanol. Ten µl of the solution were transferred to a 25 ml volumetric flask and diluted with 2, 2, 4-trimethylpentane to 10 ml, making a 1 ppm solution containing 1 ng in 1 µl which was the injection volume. This solution was diluted to give a .5 ppm solution containing .5 ng in 1 µl.

A fortified solution of 1 ppm was obtained by diluting 1 ml of the 1 mg/ml diuron in methanol solution to 1 liter with distilled water. This solution was extracted to determine percent recovery.

Atrazine Analysis

The analytical method used was a modification of the one by White et al. (61). Water samples (100 ml) were mixed with 5 grams of $MgCO_3$ - $Ca(OH)_2$ (10 to 4) to flocculate the particulate material.

Samples were vacuum filtered through Whatman No. 42 filter paper in a Büchner funnel. The filtrate was extracted with three successive 75 ml portions of chloroform. The chloroform extracts were combined and evaporated to approximately 20 ml with a gentle air stream and transferred to a basic aluminum oxide column (pyrex columns containing 10 grams of grade IV aluminum oxide) and eluted with 50 ml of chloroform-ether (95:5). The column effluent was evaporated to 20 ml and transferred to a 100 ml separatory funnel. Two ml of 50% H_2SO_4 were added, and the samples shaken gently for two hours.

Twenty ml of water were added and thoroughly mixed by shaking for 10 minutes. The aqueous layer was collected and 1 ml aliquots were removed and read on a Beckman DU spectrophotometer at 225, 240 and 255 mμ; atrazine concentrations were determined using a base-line technique of Knüsli, Burchfield and Storrs (35). Reagent blanks and samples from untreated plots were used in making background corrections. Standard curves were made using known amounts of atrazine. The limit of atrazine detection in the water samples was 0.02 ppm.

Effect of Surface Irrigation on the Lateral Movement of GS-14254 from Treated Cropland

A well established, uniform stand of furrow irrigated alfalfa was selected on the Utah State University South Farm for this study. The crop was established with irrigation furrows in alternating rows to allow for irrigation as is commonly practiced in the area. The soil type was a Nibley clay loam with 3.2% organic matter and a pH of 7.6. The percentages of clay, silt and sand were 35.5, 61.8 and 2.7, respectively. The cation exchange capacity was 23.7 meq/100 gm oven-dry soil.

The treatments consisted of two rates of herbicide and a control. The treatments were arranged in a randomized block design with three replications. After the first cutting of alfalfa was removed, the field was furrowed to prevent any crossover of irrigation water between rows. Each plot was 8 x 50 ft. GS-14254 (2-methoxy-4-s-

butylamino-6-ethylamino-s-triazine) was applied to the plots on July 2, 1971, at 1.5 and 3.0 lb/A with a bicycle sprayer having 8003 nozzle tips. It was applied at 35 psi pressure and equivalent to 19 gallons of water per acre. The plot was sprinkled with approximately 0.25 inch of water over a 2.5 hour period to both fix and leach the chemical into the soil.

The field was irrigated four days later with 1.25 inch irrigation tubes regulated to permit the water to run down the furrows at about 300 feet per hour. Water samples were collected in 110 ml sampling bottles from the first water reaching the sampling points at 0, 10, 50, and 120 feet below the end of the plots. A second sample was collected at the end of the plots after 10 minutes. Prior to the collection of samples, the sample bottles were washed with soap and rinsed four times with water. To prevent microbial degradation of the chemical, collected samples were stored in a cooler at 4^{o} C until they were analyzed.

The chemical extraction procedure used was a modification of a Geigy Agricultural Chemical extraction procedure (19) for extracting chlorotriazines from water. A 50 to 100 ml sample of water was extracted three times with 13 ml portions of chloroform in a separatory funnel. The chemical was then converted from methoxytriazine to hydroxytriazine following the procedure outlined by Geigy Agricultural Chemical Corporation for the hydrolysis of methlthiotriazine residues with several modifications. Following extraction, the chloroform was evaporated to dryness in 18 by 150 mm test tubes in a Buchler Rotary Evapo-Mix. Five ml of 1N H_2SO_4 was added to each test tube and placed in a boiling water bath for three hours. After the tubes had cooled to room temperature, the acid solution was transferred to a 250 ml separatory funnel and washed with 10 ml of 20% diethyl ether in chloroform. The organic layer was drained off and the aqueous layer was washed by shaking with 10 ml of diethyl ether. All extractions and washings followed a one minute vigorous shaking and separation period. The aqueous layer was then transferred to a three ml silica cell and the adsorbancy was measured and recorded on a Beckman DB-G grating spectrophotometer at 225, 240, and 255 mμ. The net absorbance (E) was then determined at 240 mμ by using a baseline technique according to the following equation:

$$E = A^{240} - (A^{225} + A^{255})/2$$

where A^{225}, A^{240}, and A^{255} are the absorbancies at 225, 240, and 255 mμ, respectively.

A standard curve was made by running known amounts of GS-14254 through the same hydrolysis procedure as the field samples. This standard curve was used for determining the ppm of GS-14254 in the water. Reagent blanks were run simultaneously with the standards and samples. The minimum level of detection of GS-14254 in water was 0.04 ppm.

Movement of Hormone-Type Herbicides in Surface Waters Following Field Application

In the spring of 1969 two experimental sites were selected and treated with a 1 lb/A dosage of picloram and monitored for a period of sixteen months thereafter.

One site was located in Wasatch County approximately three miles southeast of Heber City, Utah. The site consisted of a small drainage area (approximately 4 acres) that was isolated in a small draw and free from surface flowing water in the surrounding area. A small wash led from the drainage and emptied into Center Creek approximately two miles away. The treatments were made on May 7, using a truck-mounted boom sprayer and 8003 nozzle tips. The area varied in slope from approximately 3 percent to 10 percent or more near the upper side. The potassium salt of picloram was applied broadcast in 16 gpa water; an attempt was made to spray the complete watershed with the 1 lb/A rate of picloram. The collection points were established 10, 100 and 1000 meters below the treated area and the watershed was situated in such a way that nearly all of the runoff would pass the 10 meter collection point. A very small amount of runoff from adjacent areas may have entered the wash at the 100 and 1000 meter distance. One liter samples were taken from a small metal container placed in the bottom of the wash to collect the water. Duplicate samples were taken and collections were made by the landowner during periods of natural precipitation. Water samples were taken in opaque jars and refrigerated until they were processed. All analysis were performed within 48 hours after collection.

An eight-acre watershed was treated with the potassium salt of picloram at a dosage of 1 lb/A near Trenton, Utah. The site consisted of a single isolated slope covered with a mixed stand of grasses and perennial weeds. Approximately 80 percent of the area was treated

using a truck-mounted boom sprayer delivering a volume of 16 gallons of water per acre. The drainage tapered toward a small drainage ditch at the lower side and was free of any outside surface flowing water. The drain ditch emptied into the Trenton irrigation canal approximately three-fourths of a mile below the watershed. Water samples were taken in duplicate in 1 liter opaque jars and coincided with periods of natural precipitation of sufficient intensity to cause runoff. Collections were made four times during the 1969 summer season.

In 1971 a series of experimental trials were established to test the movement of picloram, 2,4-D and 2,4,5-T. The experimental area was located approximately eight miles northwest of Evanston, Wyoming. The general area is characterized by many miles of undulating foothills rising 50 to 100 feet above the broad valley floors with numerous creeks fed year-around by the Wasatch range. The foothills selected for these studies had a well deliniated north drainage slope and a south drainage slope. The south facing slope was selected for its numerous small, well defined drainageways that emptied into Duck Creek approximately 1.2 miles to the south. The four experimental sites were similar in size, slope and vegetation and were about one-half mile apart. The predominate soil type was a loam with slightly less than 1 percent organic matter content. All the drainages tapered sufficiently to allow a collection site such that essentially all the runoff water would pass through. Additional collections were made in the washes which extended to Duck Creek.

Site I consisted of two small adjacent drainages; one drainage was (~ 2.0 acres) treated with 1 lb/A picloram using the truck-mounted sprayers. Site II was established as a replicate of Site I; one drainage (~ 2.0 acres) received a dosage of 1 lb/A picloram and the second drainage (~ 2.5 acres) was treated with picloram at a 2 lb/A rate.

Sites III and IV were used to test the movement of 2,4-D and 2,4,5-T. Site III consisted of one drainage (~ 5.5 acres) treated with a tank-mix of 2,4-D at 2 lb/A plus 2,4,5-T at 1 lb/A and a second drainage (~ 2.5 acres) treated with 4 lb/A 2,4-D plus 2 lb/A of 2,4,5-T. The treatments made on Site III were repeated on Site IV with one watershed (~ 1.5 acres) receiving the 2 lb/A rate of 2,4-D plus 1 lb/A 2,4,5-T and a second watershed (~ 1.25 acres) treated with the combination of 2,4-D and 2,4,5-T at the highest rates.

The picloram, 2,4-D and 2,4,5-T treatments were applied June 29 and a rainstorm occurred one week later that deposited 1.56 inches of rain in a three-day period. Duplicate 3 liter samples were collected

from each of the collection points during the runoff period of the storm. The samples were immediately cooled on blocks of CO_2 and transferred to the laboratory where they were refrigerated and processed within seven days. Quantitative determinations were made in triplicate on each sample.

Picloram Analysis

The picloram content of the water samples was determined chromatographically using a Varian Aerograph Model 1800 chromatograph equipped with a tritium electron capture detector and a five foot stainless steel column with an inside diameter of 1.8 mm packed with SE-30 oil on 80/100 mesh Chromosorb Q. Purified nitrogen at a flow rate of 60 ml per minute was used as the carrier gas. The injector, column and detector temperatures were 225, 195 and 215° C, respectively.

The method of Merkle, Bovey and Hall (44) with minor modifications was used to determine the picloram concentration in 500 ml samples of water. The samples were made basic with KOH and reduced to about 250 ml on a hotplate. The concentrated sample was acidified to pH 2.0 with HCl and extracted twice with 100 ml portions of diethyl ether. The ether extracts were combined and evaporated to ~ 1.0 ml on an evaporator. The methyl ester of picloram was made by reacting it with 8 milliliters of boron trifluride in methanol. Ten ml of water was added and the solution was transferred to a separatory funnel and washed with an equal volume of hexane. The two phases were thoroughly mixed and allowed to separate. The organic phase was collected and used to inject into the chromatograph. As determined in our laboratory, the lower limit of detection by this method was 3 to 4 ppb picloram. Plant bioassays were used for qualitative measurements of picloram in the runoff waters. The technique verified the quantitative determinations of other methods but was noticeably inferior to GLC at the lower concentration levels. Safflower plants were grown in greenhouse pots in 500 gm of silt loam soil. When the plants reached a height of 4 inches the runoff water taken from the field was used in the normal watering routine; approximately 25 ml was added to the soil every third day. Water of known picloram concentrations was used to develop rate-response curves for comparison.

Picloram concentrations were verified in most field samples by an abbreviated analytical procedure developed by the authors and described in Appendix B.

Phenoxy Herbicide Analysis

Water samples containing 2, 4-D and 2, 4, 5-T were brought to pH 10.0 with NaOH according to the method of Frank and Comes (17) and extracted with chloroform after acidification to pH 2.0 with HCl. The 2, 4-D was removed from the chloroform with 0.1 N sodium bicarbonate and, after acidification to pH 2.0, was again extracted with chloroform. The chloroform was evaporated to dryness and the methyl ester was made by reacting the residue with diazomethane in ethyl ether and taken up in isooctane. The two compounds were separated by gas chromatography on a 5 foot column packed with 60/80 mesh Chromosorb W coated with 10% QF-1 over 0.5% Carborwax 20-M. Two procedures were followed to check the identity of the two herbicides in the water samples. A 5 foot column prepared with 5% SE 30 on Gas Chrom Q was used as a second method to resolve the compounds. The 2, 4-D and 2, 4, 5-T contents were determined by comparing the peak height produced to that produced by known quantities of the individual herbicides. The recoveries from water were 96 and 90 percent for 2, 4-D and 2, 4, 5-T, respectively. The lower limit of detection was approximately 50 ppb for each herbicide.

Laboratory Studies

Stock solutions containing 0.05 to 10 ppm of ^{14}C-labeled picloram (carboxyl - ^{14}C, specific activity 4.13 μc /mg) were prepared in deionized water. Calibration curves were made by counting aliquots of the stock solutions on a Packard TriCarb liquid scintillation counter according to the method of Yaron, Swoboda, and Thomas (62). One ml aqueous sample was added to 19.0 ml of liquid scintillator, dissolved by slight shaking and counted for at least three 10-minute periods. Radioactivity was usually high and the counting efficiency was approximately 65 percent or better. The counting error was ± 3 percent.

A preliminary experiment was performed to check any picloram adsorption on glass containers, polypropylene centrifuge tube walls, rubber corks, or degradation by sunlight. Twenty-five ml of each of

the stock solutions were exposed to the containers for a 30-day period. As a precautionary measure, all subsequent experiments were conducted in a dark room, because the actual handling of samples subjected them to different light conditions from one experiment to another.

To check for degradation of picloram during the course of an experiment, a thin layer chromatography (TLC) technique was used. A 100 λ sample (column effluent in case of column studies) was applied to the TLC plate in quadruplicate. The TLC plate had a coating, 250 μ thick, of Silicic AR TLC - 7GF, a neutral sorbent produced by Mallinckrodt, which contained approximately 84 percent silicic acid, 10 percent $CaSO_4$, and 6 percent Phosphor.

The developing solvent was benzene:acetic acid (152:48). TLC plates were viewed under UV light. Portions of adsorbent containing the spot were scraped with a clean spatula into a scintillation vial, scintillation fluid added, and counted, along with samples of known radioactivity. Portions of TLC plates, with their R_f values corresponding to known degradation products of picloram, were also counted. Samples were applied to TLC plates immediately after elution from the column, along with samples of known radioactivity.

Factors Affecting Soil Adsorption-Desorption of Picloram (Batch Studies)

A series of experiments were conducted to determine the influence of incubation time, soil type, organic matter, herbicide concentration, pH, and inorganic salts on the soil adsorption and release of picloram. A slurry technique (25) was used throughout the series and quantitative determinations of the herbicide were made primarily by using radiolabelled picloram. The following procedures were common to all experiments unless otherwise noted.

Ten grams of air-dried (5 grams for Chance and Aiken soils) 60-mesh soil were weighed into a polypropylene tube and 10 ml of herbicide solution added. The tubes were stoppered and placed on a mechanical shaker in a constant temperature bath until equilibrium was reached or for the indicated time. After shaking, the slurry was centrifuged at 1500 RPM for 10 minutes. A 1 ml aliquot of the supernatant was taken at various intervals and counted. The herbicide adsorbed was determined by subtracting the concentration found in the supernatant

from the initial concentration. The temperature fluctuation in the water bath was $\pm 0.3^{\circ}$ C. All determinations were made in duplicate. Five soils were used for these experiments. Important characteristics of these soils are described in Table 1.

Effect of time on adsorption-desorption of picloram was investigated by the above mentioned slurry technique by taking aliquots after each 6-hour interval, except in Aiken soil where samples were taken at 1/2-hour intervals. When no change in the picloram concentration of the supernatant was observed, it was assumed that equilibrium had been reached. Similar procedures were followed for desorption, except the time interval for sampling was generally four hours.

One experiment was designed to determine the influence of soil type and organic matter on soil adsorption of picloram. Organic matter was removed from the soil by heating to 350° C for 24 hours in an electric furnace. Adsorption of picloram by the five soils was determined after removing the organic material by using the slurry technique.

Desorption of picloram was studied utilizing the following technique. Adsorption equilibrium was allowed to take place and 1 ml sample of the supernatant was taken after centrifuging the sample. Ten ml water was added and the system was allowed to re-equilibrate; the tubes were centrifuged and a 1 ml aliquot was again taken from the supernatant for analysis. To study the effect of dilution on desorption of picloram, the soil-solution was diluted with additional water after adsorption equilibrium. They were allowed to re-equilibrate for 24 hours and 1 ml samples were withdrawn from the supernatant for counting.

The influence of herbicide concentrations on adsorption of picloram was studied using picloram concentrations ranging from .05 to 10 ppm and following the procedure outlined above.

Four different temperatures (17.7° C, 25° C, 28.2° C, 34.7° C) were used with Providence and Chance soils and three temperatures (17.7° C, 25° C, and 34.7° C) were used with Aiken soil to study the effect of temperature on adsorption and desorption of picloram.

Another experiment was designed to determine the effect of pH on adsorption of picloram by Providence and Chance soils. The pH change was induced by adding either KOH or HCl. Twenty-four hours were allowed for equilibration. The pH effects above pH 9.2 in Providence soil and above pH 8.5 in Chance loam could not be studied

Table 1. Properties of soils used in the studies.

Soil type	pH	Organic matter %	Air dry moisture %	Sand[a] %	Silt %	Clay %	Sesqui-oxides %	$CaCO_3$ equiv. %	Cation exchange capacity meq/100 gm	Picloram dissociated in water[b] %
Nibley silty clay loam	7.35	2.53	2.62	3.4	59.6	37.0	6.9	2.1	25.7	99.94
Millville silt loam	7.55	1.90	1.14	14.9	65.7	14.9	5.2	28.0	15.6	99.96
Chance loam	6.50	18.70	4.76	34.6	53.3	19.1	5.1	0.0	37.0	99.60
Aiken clay	6.45	0.60	4.48	27.2	32.6	40.2	21.7	0	16.3	99.56
Providence silt loam	7.05	3.59	1.92	31.6	53.1	15.3	5.2	0	30.5	99.89

[a] includes 2 to 0.05 mm fraction

[b] based on a pKa of 4.1 (Hamaker, Goring, and Youngson, 1966) for the dissociation of H^+ from the carboxylic group

because of solubilization of organic matter by the high alkalinity and consequent interference during scintillation counting.

The influence of several salts on adsorption of picloram onto the Providence soil was investigated. Dilute solutions (1 to 5 meq/l) of KCl, K_2SO_4, $CaSO_4$, and $CaCl_2$ were used, and their influence on picloram adsorption was studied using the slurry technique. A preliminary test using concentrations of 66 meq/l and 660 meq/l $BaCl_2$ was performed. The effect of $CaCl_2$ concentrations on the adsorption of picloram by the other four soils was examined at 0, 5, 10, 25, 50, and 5000 meq/l.

Mechanical analyses (particle size distribution) and organic matter analyses were performed by the Utah State University Soil Testing Laboratory. The former was based on a method adapted from Kilmer and Alexander (33). The latter was adapted from the Walkley-Black wet digestion method of Allison (4).

Cation exchange capacity (CEC) was determined by the method of Chapman (11) by the Utah State University Soil Testing Laboratory.

Factors Affecting Soil Adsorption-Desorption of Picloram (Column Studies)

Columns used in this study were made of pyrex glass, 2 cm diameter, with fitted glass bottoms. There was a narrow outlet at the center of the bottom of each column. Soil was packed into the column to depth of 14.5 cm. Soil in the column was saturated with deionized water to eliminate air in the column by gradually immersing the column into water in a graduated cylinder and leaving it until free water appeared on the top of the soil column. Deionized water was then passed through the soil from the top for 24 hours before the herbicide was added. The soil column contained glass beads to a depth of about 0.5 cm at the top of the soil to prevent the soil from puddling.

After the soil had been washed free of herbicide at the end of the experiment, the same column was used to determine the dispersion coefficient (D_o). A solution of 0.1N $CaCl_2$ was used to obtain the Cl^- breakthrough curve (BTC). The dispersion coefficient was calculated from the Cl^- BTC according to the following equation:

$$\frac{\partial C}{\partial t} = - v_o \frac{\partial C}{\partial Z} + D_o \frac{\partial^2 C}{\partial Z^2}$$

where C is the concentration of herbicide in solution, t is time, Z is the distance along the column, v_o is the interstitial flow velocity, and D_o is the dispersion coefficient.

The chloride concentration was determined by the potentiometric titration with 0.01N $AgNO_3$. A Corning Model 12 pH meter with an expanded scale was used; the electrodes were a double junction reference electrode and a silver billet indicator electrode.

A Heath Recording Electrometer Model Eu-20-11 was used to monitor flow rates from the column. The average interstitial flow velocity (v_o) was obtained by averaging the pore-water velocities for different column effluent fractions (3 ml each). There was a slight decrease in flow rate over the period of a particular experiment; a typical breakthrough curve for Millville silt loam soil is shown in Figure 1.

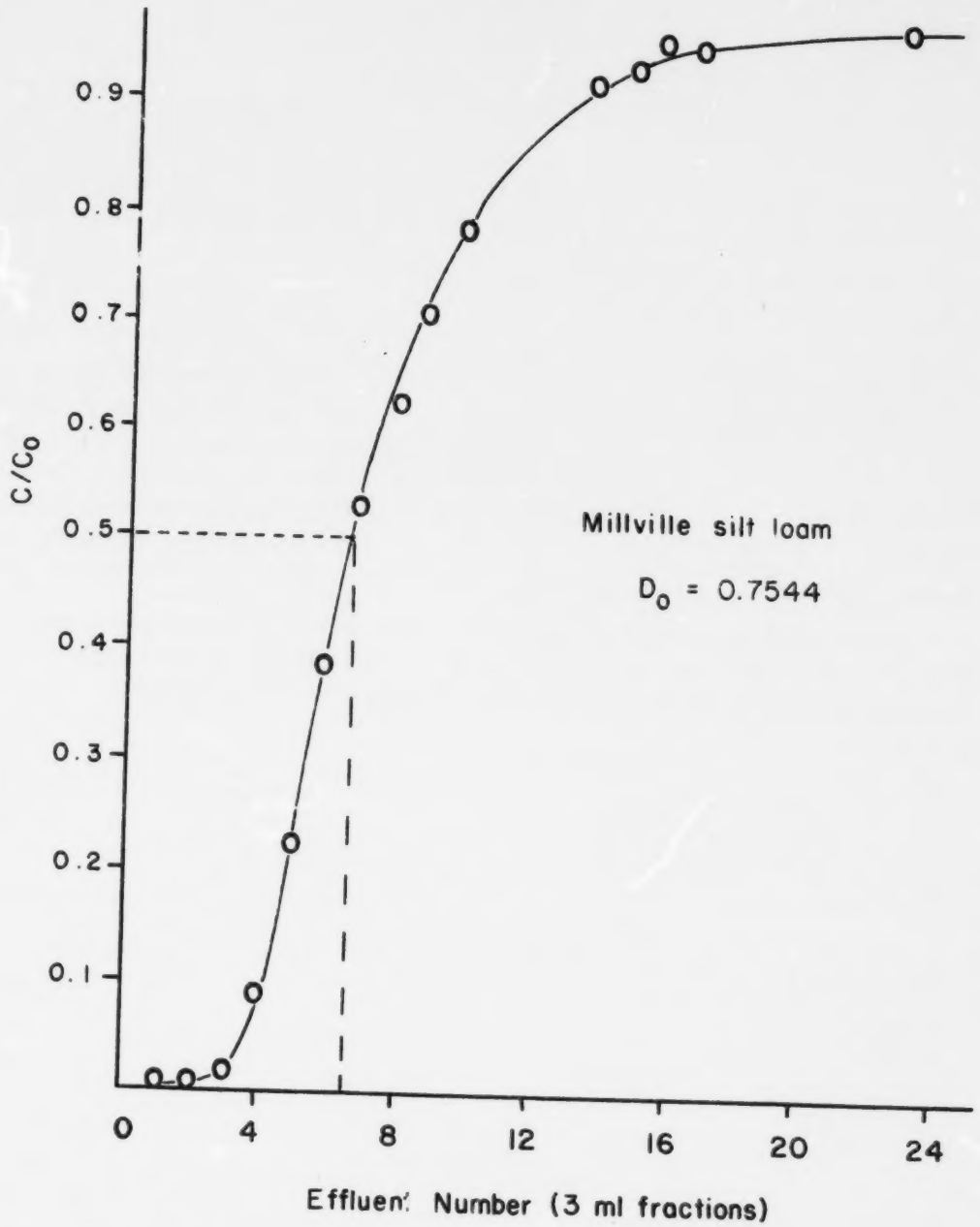

Figure 1. A typical Cl^- breakthrough curve (BTC) used for calculating dispersion coefficient.

SECTION VI

RESULTS AND DISCUSSION

Field Experiments

Movement of Herbicides Following Heavy Applications to Canal Banks

Water samples were taken as the initial flush of water crossed the treated plots and reached the collection points. The highest average concentration of diuron in the water taken from the Trenton canal was 1.78 ppm (Table 2). This concentration was the average of four determinations ranging from a high of 1.89 ppm to a low of 1.47 ppm and taken at a distance of 10 feet below the treated plots. The concentration of diuron in the runoff water was greatest at the collection point nearest the treated area and dropped rapidly when the samples were taken further down the canal. The limit of detection using the method of McKone and Hance (41) was .02 ppm when the untreated canal water was used to prepare the calibration standards.

Table 2. Diuron concentration (ppm) in irrigation canal water at 10, 100 and 1000 foot distances below areas receiving a 30 lb/A dosage to control ditchbank vegetation.

Canal	Distance below treated site (ft)	Diuron concentration (ppm)*	
		(First flush)	(Part capacity)**
Trenton	10	1.78	<0.02
	100	0.93	<0.02
	1000	<0.02	<0.02
North Logan	10	0.72	<0.02
	100	<0.02	<0.02
	1000	<0.02	<0.02

* Average of four determinations

**Approximately 90 percent in the Trenton canal and 60 percent in the North Logan canal

A similar pattern of diuron movement was observed in the North Logan canal. The highest concentration of diuron was observed in samples taken 10 feet below the treated plots but was not detectable in the samples taken 100 or 1000 feet from the treated area. The average diuron concentration in the North Logan canal water samples taken 10 feet below the plots was 0.72 ppm compared to 1.78 in Trenton. The two canals differed in vegetative cover at the time of treatment which may influence the quantity of herbicides moving in the surface water.

Most of the samples analyzed contained less than 0.02 ppm diuron. Chancellor (10) found that diuron concentrations up to 180 ppm are nonpoisonous to man and livestock; it also has a low toxicity to fish. Even at 1.89 ppm, the highest concentration of diuron in water in this study, there is very little chance that injury to fish, livestock, or plants would result from treating the canal banks for the control of undesirable plant species.

Atrazine demonstrated a very small tendency to move in irrigation canal waters when used as a ditchbank spot treatment at the end of a cropping season. It appears reasonable to assume that its potential to move with the water would be greatly increased if it were used immediately prior to filling the channel with water.

Atrazine movement appeared greatest in the Trenton canal as compared to the North Logan canal probably due to the difference in vegetative cover. The average atrazine concentration in water taken 10 feet below the plots was 0.86 ppm at Trenton and 0.44 ppm in the North Logan canal (Table 3). The samples collected 100 feet below the plots averaged 0.72 ppm atrazine in the Trenton canal while no detectable level was observed in the 100-foot samples collected in North Logan. Atrazine was not found in the initial water flush samples collected 1000 feet below the treated areas in either canal. Samples collected on the same day but after the canals had received most of their capacity of water did not reveal any measurable quantity of herbicide.

Atrazine movement in these studies was considerably lower than that reported by White et al. (61). In their study, however, application was made 1 hour and 96 hours prior to wash-off. The samples were not taken in the present study for a period of approximately six months after the application. The smaller quantity of atrazine moving is probly due to several interacting processes. Adsorption and leaching into the soil profile during the time between treatment and sample collection would cause the herbicide to be less available for movement in the surface water and would also allow for degradation of the herbicide.

Table 3. Atrazine concentration (ppm) in irrigation canal water at 10, 100 and 1000 foot distances below areas receiving a 10 lb/A dosage to control ditchbank vegetation.

Canal	Distance below treated site (ft)	Atrazine concentration (ppm)* (First flush)	(Part capacity)**
Trenton	10	0.86	<0.02
	100	0.72	<0.02
	1000	<0.72	<0.02
North Logan	10	0.44	<0.02
	100	<0.02	<0.02
	1000	<0.02	<0.02

* Average of four determinations

**Approximately 90 percent in the Trenton canal and 60 percent in the North Logan canal

Atrazine and diuron concentrations in surface water shown in Tables 2 and 3 are probably of the magnitude encountered normally since the recommended procedure is to allow a 4 to 6-month interval to immobilize the herbicides in the soil prior to using the canal for irrigation. Previous studies (61) have also shown that the major portion of atrazine in wash-off is contained in the water fraction as opposed to that adsorbed onto the soil particles in the wash-off material; consequently, the herbicide concentrations shown in Tables 2 and 3 would not change significantly if the quantity of atrazine in the sediment was added to each determination.

Effect of Surface Irrigation on the Lateral Movement of GS-14254 from Treated Cropland

The average levels of GS-14254 in irrigation water declined rapidly with increased distance from the treated plots (Table 4). The irrigation return flow from the plots treated with 2.0 lb/A GS-14254 consistently had higher residue levels than that from the plots treated with 1.5 lb/A (Table 4). The differences in residue levels between treatments at equal distances from treated plots were significant at the 10% probability level. The average GS-14254 concentration in the irrigation water for the 1.5 lb/A treatment ranged from .272 ppm at

the end of the treated plots to .005 ppm at 120 feet from the treated plots. For the 3.0 lb/A treatment, GS-14254 concentrations ranged from .487 ppm at the end of the plots to .035 ppm at 120 feet from the plots (Table 4).

Table 4. A comparison of the quantity of GS-14254 recovered in the runoff water from two treatments at different distances from the treated area.

Distance (feet)	Rate of GS-14254 applied (lb/A)	Concentration in runoff (ppm)[a]
0	1.5	.272 a
	3.0	.487 b
10	1.5	.122 c
	3.0	.147 c
50	1.5	.013 d
	3.0	.053 d
120	1.5	.005 d
	3.0	.035 d

[a] Values followed by the same letter are not significantly different at the 5% level as determined by the L.S.D. test. Each value is the mean of three replications.

Residue levels in the runoff water dropped off rapidly with time. Table 5 shows that the concentration of GS-14254 in the first flush of water was .272 ppm for the 1.5 lb/A rate and that it dropped off to .010 ppm in the water passing the same point 10 minutes later. It also shows that the concentration in the first flush of water was .487 ppm for the 3.0 lb/A rate and that it dropped off to .043 ppm after 10 minutes.

These data agree with the runoff studies conducted by White et al. (61) on the loss of atrazine from fallow land. They found that losses were highest during the early stages of runoff followed by a gradual tapering off.

Table 5. A comparison of the quantity of GS-14254 recovered in the runoff water at the end of the treated plots from two treatments at different times during irrigation.

Time (min)	Rate of GS-14254 applied (lb/A)	Concentration in runoff (ppm)[a]
0	1.5	.272 a
	3.0	.487 b
10	1.5	.010 c
	3.0	.043 c

[a] Values followed by the same letter are not significantly different at the 5% level as determined by the L. S. D. test. Each value is the mean of three replications.

Losses of GS-14254 due to erosion were not included in this study. It was estimated that the 110 ml water sample contained 1 to 2 gm of soil. White et al. (61) stated that the concentrations of atrazine in the soil fraction were much higher than in the water fraction (the ratio of concentration of atrazine in the soil to atrazine in the water was about 10 to 1). However, due to the greater amounts of water that were lost as compared to soil, there were about 10 times as much atrazine lost in the water as in the soil fraction. Although no measurement of the level of GS-14254 was made in the soil fraction of the water sample, a similar 1 to 10 ratio might be expected since the two herbicides have similar solubilities and soil adsorption characteristics.

GS-14254, like atrazine, will move in irrigation or precipitation runoff. The concentration of GS-14254, however, drops off rapidly with increased distance from the treated areas (Table 4). In areas where s-triazine sensitive crops are grown, phytotoxicity symptoms might occur on sensitive plants from runoff from treated areas.

Movement of Hormone-Type Herbicides in Surface Waters Following Field Application

Table 6 shows the concentration of picloram in surface waters from an area treated with picloram at 1 lb/A following four periods of natural precipitation. At the time of the first collection there had been 0.25 inch of rain on the Wasatch experiment. It was sufficient rain to move water across the site and allow collection of water at various intervals below the treated site. Picloram was detected in surface waters at 10 and 100 meter distances below the treated area; the concentrations of picloram were 28 and 21 ppb, respectively. Collections made at distances greater than 100 meters did not contain detectable amounts of the herbicide.

Table 6. Average picloram concentration in surface runoff water at various collection points during 1969.

Site	Collection date	Precipitation after treatment, inches (cumulative)	Concentration (ppb)* Location (meters from treated area) 10	100	1000
Wasatch County	May 16	0.25	28	21	0
	June 26	2.32	3	10	0
	July 20	2.80	0	T**	0
	Aug. 17	4.08	0	0	0
Cache County	May 15	0.20	10	8	T**
	June 16	1.10	0	0	0
	June 27	3.55	0	0	0
	July 8	4.04	0	0	0

* Each value is the mean of six determinations
**T = Trace

A second period of storms occurred on June 26, 1969, and produced runoff from the treated area. Only the waters collected at 10 and 100 meter distances contained measurable amounts of picloram. A concentration of 3 ppb was observed in the water 10 meters below the site and 10 ppb was measured in moving water 100 meters below the

experiment. This small increase in concentration from 10 to 100 meters was primarily due to one of the triplicate samples taken at 100 meters being quite high. Subsequent samples taken in July and August in 1969 and throughout the 1970 season failed to produce measurable quantities of the herbicide in runoff waters.

A similar experiment was conducted in Cache County, Utah to evaluate the influence of soil type and vegetation on picloram movement. Samples of runoff water from the first major rainstorm demonstrated some picloram movement. Ten ppb picloram was observed in the samples taken 10 meters below the treated area and 8 ppb picloram was observed in water taken 100 meters below the plot (Table 6). It was not possible to detect measurable quantities of the herbicide at distances greater than 100 meters from the treated area during the first collection period, nor was it possible to detect picloram in any samples taken during succeeding rainstorms during the 1969 season. The experiment was monitored for picloram movement during the 1970 season and no picloram was detected in the surface waters.

Bioassay with safflower plants confirmed quantitatively the results obtained with chromatographic analysis of water samples. The bioassay technique also demonstrated the presence of a significant amount of picloram in the soil within the boundaries of the treated site throughout the course of the experiment.

Four experimental sites were selected in 1971 and treated as shown in Tables 7, 8, and 9. The four sites were located in Rich County, Utah. The sites consisted of four similar well-defined small watersheds with a medium stand of rabbitbrush (Chrysothanmus nauseosus) and grass species. Total precipitation during the initial storm was 1.56 inches; precipitation during the remainder of the summer months was not adequate to allow collection of runoff samples.

Table 7 shows the picloram concentrations in the surface runoff collected at various distances from the two sites treated with picloram. Picloram was found in surface runoff waters adjacent to areas treated when rainfall was sufficient to result in runoff from the treated areas within a 7-day period after application of the chemicals. Higher concentrations were observed below Site I than were observed below Site II (Table 7) probably due to increased vegetation on Site II and slight differences in soil characteristics. Concentrations observed below Site I ranged from 1082 to 17 ppb at 10 and 1000 meter distances below the plot treated with 1 lb/A dosage of picloram. Runoff water collected at the various distances below the 2 lb/A

Table 7. Picloram concentrations (ppb) in surface runoff waters collected at several distances from herbicide treated sites.

Location	Rate (lb/A)	Acres treated	% of watershed	Concentration of Picloram (ppb)* Distance from treated site (meters) 5	10	100	1000
Site I (Rich County)	1.0	1.1	54	1082	771	58	17
	2.0	1.2	83	2716	1851	51	0
Site II (Rich County)	1.0	1.6	84	561	486	29	0
	2.0	2.1	85	512	312	78	0

*Each value is the mean of six determinations

Table 8. 2, 4-D concentrations (ppb) in surface runoff waters collected at several distances from treated areas.

Location	Rate (lb/A)	Acres treated	% of watershed	Concentration of 2, 4-D (ppb)* Distances from treated site (meters) 5	10	100	1000
Site III	2	2.4	43	1610	1810	830	210
(Rich County)	4	1.7	67	4210	3710	1260	100
Site IV	2	1.2	83	3240	2750	670	220
(Rich County)	4	1.1	86	4170	3120	1150	120

*Each value is the mean of six determinations

Table 9. 2, 4, 5-T concentrations (ppb) in surface runoff waters collected at several distances from treated areas.

Location	Rate (lb/A)	Acres treated	% of watershed	Concentration of 2, 4, 5-T (ppb)* Distances from treated site (meters) 5	10	100	1000
Site III	1	2.4	43	850	580	120	0
(Rich County)	2	1.7	67	1380	1020	110	T
Site IV	1	1.2	83	1010	420	80	0
(Rich County)	2	1.1	86	1260	590	10	0

*Each value is the mean of six determinations

treatment of Site I had a greater quantity of herbicide than those collected below the area treated at a 1 lb/A rate of picloram as shown in Table 7. Nearly equal amounts of picloram were recorded in the surface waters collected at various distances below Site II from the 1 lb/A and 2 lb/A treatments. On this site, application rate did not influence the quantity of herbicide moved; the additional vegetation on the site may have limited the quantity of herbicide available for movement. After 12 weeks, the picloram concentration had decreased to 1 ppb or less at all sampling points. Within 1 year the concentrations of picloram in runoff water remained below the limit of detection of the analytical methods used.

The movement of 2,4-D in surface waters was determined after treating two watersheds with a tank mix of ester formulations of 2,4-D and 2,4,5-T. Treatments were made on June 29, 1971, using the same procedure as was used on the picloram sites. Only one rainstorm produced runoff sufficient for analysis during the summer season and consequently only one sampling of 2,4-D concentration is reported in Table 8. Each value is the mean of the two samples collected at each of the collection points during the initial runoff period.

Where 2,4-D was applied at 2 lb/A on Sites III and IV the herbicide observed in surface runoff waters ranged from 210 ppb at 1000 meters below the plot to 3240 ppb at a 5 meter distance below the plots. No detectable amount of 2,4-D entered the native stream slightly more than 1.6 Km from the experimental sites. Likewise, no detectable levels of 2,4-D were observed in surface water in the fall of 1971 nor during the growing season of 1972. The dosage of 2,4-D influenced the amount of herbicide loss; however, this differential was more pronounced on Site III than on Site IV. Table 8 shows that the loss of 2,4-D from Site III nearly doubled as the rate of application was doubled. Only a slight increase in 2,4-D movement was observed when the dosage of 2,4-D was doubled on Site IV. Thus the rate of application must be considered in relation to soil texture and vegetative cover in predicting the surface movement of herbicides. As vegetative cover decreases, more herbicide is deposited on the soil surface and consequently more readily moved in the surface waters, this would probably be more likely in the sandy soils as opposed to heavier soils.

Similar movement patterns were observed with 2,4,5-T as were found for 2,4-D. The lower quantities observed were probably a result of the lower dosages applied in the case of 2,4,5-T. The concentration

of 2, 4, 5-T in runoff waters ranged from approximately 100 ppb adjacent to the plots as shown in Table 9. There were only minor differences in the 2, 4, 5-T levels observed in water samples taken below the 1 lb/A dosage treatment plots when compared with the 2 lb/A treatment plots. The level of 2, 4, 5-T in surface waters was below the detection limit 12 weeks after application and after over-wintering. One year after applying the herbicides, no detectable amounts of 2, 4, 5-T were observed in surface waters generated as spring runoff.

Laboratory Studies

Degradation of Picloram

Various aqueous solutions of picloram (0.05 to 1.0 ppm) were exposed to normal amounts of sunlight in the laboratory for a 12 day period. No degradation was noted as determined by TLC and liquid scintillation counting. Adsorption onto walls of the reaction containers was shown to be extremely small and no adjustments were deemed necessary.

Factors Affecting Soil Adsorption-Desorption of Picloram (Batch Studies)

As shown in Figure 2, adsorption equilibrium for picloram was attained after about 50 hours by Millville and Nibley soils, and was nearly complete for the Providence soil within 120 hours. Aiken soil attained equilibrium within 4 hours (not shown in Figure 2). Chance loam soil was still adsorbing after 120 hours at 34.7° C. The adsorption kinetics of soils in Figure 2 shows soils with higher organic matter took longer to reach equilibrium. Although the soils differed in many properties, organic matter appeared to account for a major portion of adsorption on these soils.

The effect of soil type and organic matter content of the five soils on the adsorption of picloram at two concentrations, 0.5 and 1.0 ppm, is given in Table 10. The adsorption ranged from 10.8 to 58.2%. Adsorption on Millville, Nibley, and Providence soils, all with similar pH values, increased with an increase in organic matter content. For each 1% increase in organic matter there appears to be about 150 μgm/kg increase in picloram adsorption. When the soil organic matter was altered or removed from the five soils by heating to 350° C,

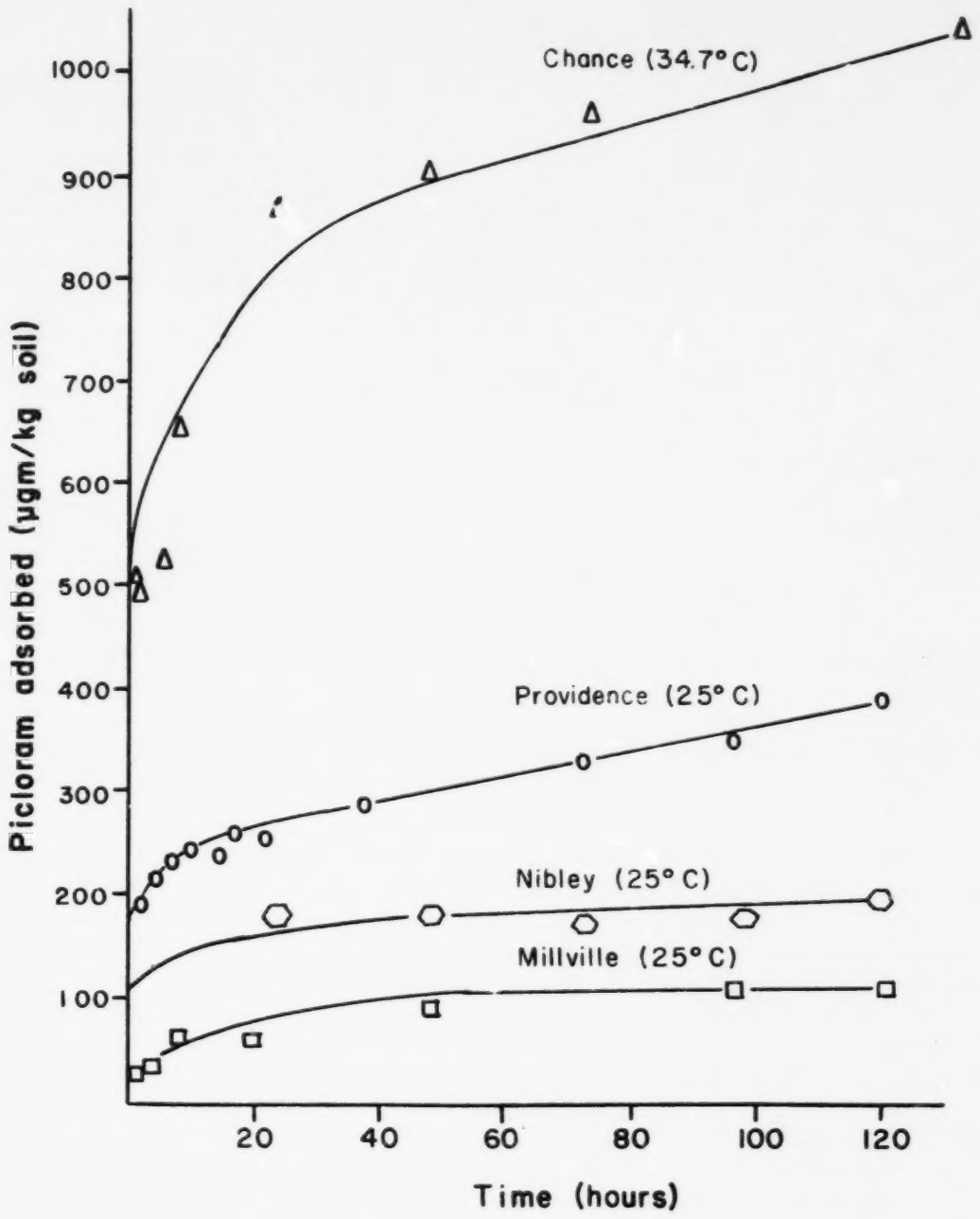

Figure 2. Effect of time on adsorption of picloram by four soils at 1 ppm initial concentration.

Table 10. Adsorption of picloram by five soils, in their natural state and after removal of organic matter. Incubations were made at 25°C and picloram concentrations of 0.5 and 1.0 ppm.

Soil	Organic matter	pH	With organic matter				Without organic matter		Reduction in adsorption	Picloram adsorbed on organic matter
			high rate[a]		low rate[b]		Amount adsorbed[c]			
	%		µgm/kg	%	µgm/kg	%	µgm/kg	%	µgm/kg	% total adsorbed
Chance loam	18.7	6.50	1042	52.1	582	58.2	144	7.2	898	85.6
Providence silt loam	3.6	7.05	371	37.1	175	35.0	49	4.9	322	88.0
Nibley silty clay loam	2.5	7.35	236	23.6	-	-	18	1.8	218	91.0
Millville silt loam	1.9	7.55	108	10.8	-	-	29	2.9	79	70.0
Aiken clay	0.6	6.45	268	13.4	135	13.5	240	12	28	10.5

[a] high rate corresponds to 1 ppm of picloram in solution

[b] low rate corresponds to 0.5 ppm of picloram in solution

[c] at high rate

a reduction of up to 91% of the total adsorption occurred as shown in Figure 3. Although Hance (?6) has noted that all of the organic matter is probably not removed by the heating procedure and that some disruption of clay minerals may occur, this experiment demonstrates the importance of organic matter in the adsorption of picloram.

The release (desorption) of picloram already in equilibrium with the soil is shown in Table 11. Desorption was accomplished by two successive washings with 10 ml portions of deionized water. The percent of picloram desorbed (of that initially adsorbed) generally decreased inversely with the amount of organic matter. This demonstrates the importance of organic matter in soils in the retention of picloram. The total picloram eluted by two water extractions was 41% to 72% of that initially adsorbed. Four extractions were performed on the Providence soil and demonstrated that after the second water extraction picloram is removed with considerably more difficulty, only 5.6% and 2.8% of adsorbed picloram was desorbed in the third and fourth extractions, respectively (Table 12).

The relationship between the adsorption of picloram and the pH of the soil suspension is given in Table 13 and Figure 4 for Providence silt loam and Chance loam soils; pH was adjusted by adding 0.1N KOH or 0.1N HCl to the soils. There was a sharp increase in adsorption as pH decreased. In Table 13, the percentage of dissolved free acid, calculated using a pKa of 4.1 for the carboxylic group is shown. Adsorption appears to increase as the undissociated acid form increases with decreasing pH. Hamaker, Goring, and Youngson (24) have recently shown a sharp increase in adsorption of picloram as the soil slurry pH is lowered from 6.5 to 4.0.

The adsorption of picloram was influenced by the pH of the soil suspension. The following regression equations show this relationship for Chance loam and Providence silt loam, respectively (Figure 4):

$$\log_{10} (\mu gm \text{ adsorbed/kgm soil}) = 3.654 - 0.107 \text{ pH}$$

and

$$\log_{10} (\mu gm \text{ adsorbed/kgm soil}) = 3.460 - 0.125 \text{ pH}$$

The correlation coefficients (0.993 for Chance loam soil and 0.985 for Providence silt loam soil) indicate that adsorption of picloram by

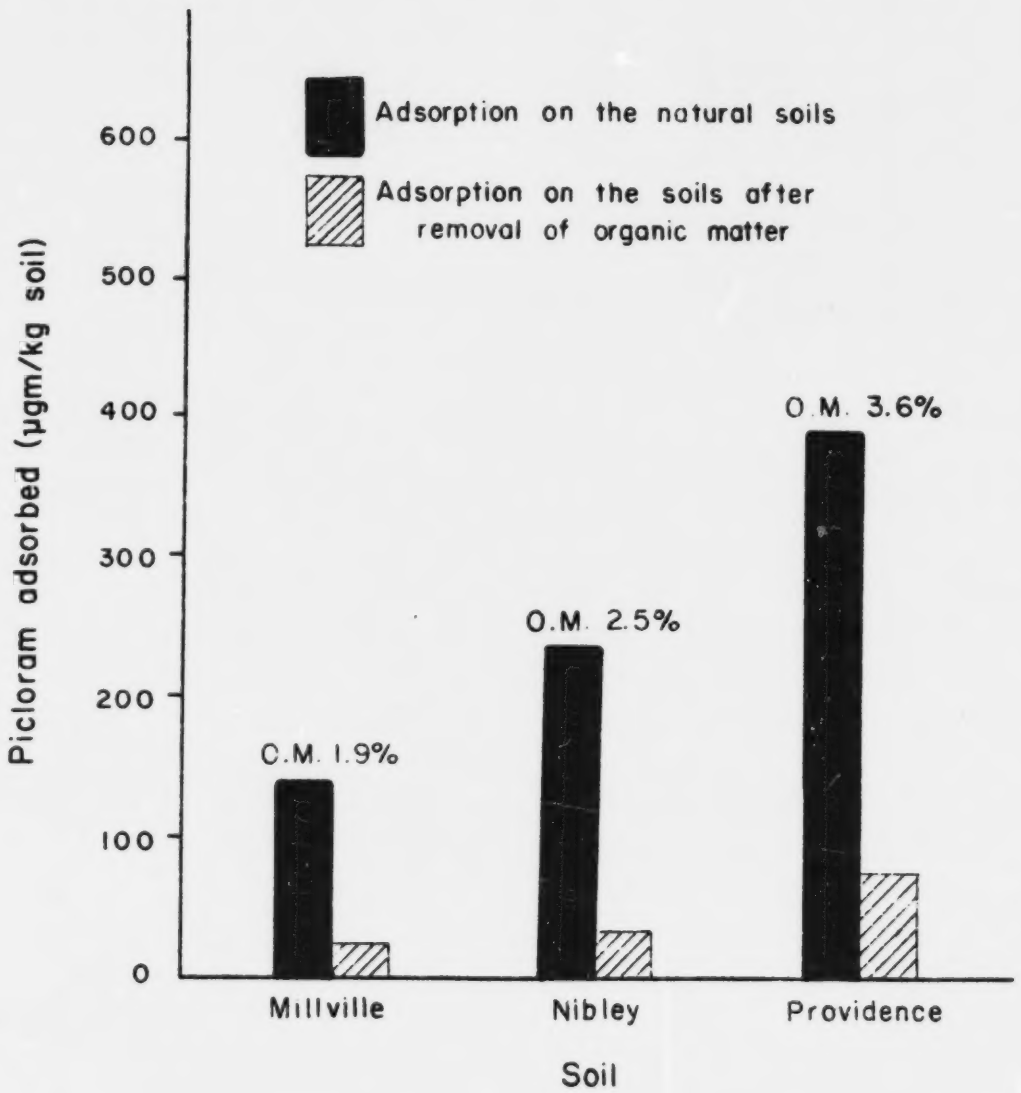

Figure 3. Effect of organic matter content of three soils and the removal of organic matter on adsorption of picloram. Adsorption determined at 25° C.

Table 11. Effect of soil type and organic matter content on the release of picloram with 10 ml extractions of deionized water at 25° C.

Soil	Organic matter	Picloram initially adsorbed	Extraction number	Picloram desorbed[a]	
	%	µgms/kgm soil		µgms/kgm soil	%initially adsorbed
Millville silt loam	1.9	108	1	69.3	64.2
			2	8.2	7.6
Total desorbed				77.5	71.8
Nibley silty clay loam	2.53	236	1	63.4	26.9
			2	58.9	25.0
Total desorbed				122.3	51.9
Providence silt loam	3.59	371	1	96.0	25.9
			2	56.0	15.1
Total desorbed				152.0	41.0

[a]Average standard deviation = 0.49

Table 12. Release of picloram from Providence silt loam soil with four successive 10 ml extractions of deionized water at 25°C. The soil contained 371 µgm picloram/kg soil initially.

Extraction number	Herbicide released				Herbicide released				Average pH
	Replicate			Average	Replicate			Average	
	1	2	3		1	2	3		
	µgm/kg soil				% of that initially adsorbed				
1	88.2	96.4	84.0	89.5	23.8	26.0	22.7	24.2	7.50
2	99.1	--[a]	44.0	71.6	26.7	--[a]	11.9	19.3	6.85
3	22.0	19.6	20.0	20.5	5.9	5.3	5.4	5.5	6.65
4	14.4	--[a]	7.0	10.7	3.9	--[a]	1.9	2.9	6.70
Total desorbed				192.3				51.9	

[a]Samples lost during extraction

Table 13. Effect of pH on the adsorption of picloram by Chance loam and Providence silt loam soils at 25° C (initial picloram concentration 1 ppm).

pH	Picloram adsorbed µgm/kg soil	Picloram undissociated %
	Chance loam soil	
3.40	1832	83.4
4.35	1584	36.0
5.15	1278	8.2
5.75	1132	2.19
6.20	962	.79
6.55	850	.35
6.90	868	.16
7.05	780	.11
7.25	764	.07
7.55	730	.04
8.00	612	.01
8.50	522	.004
	Providence silt loam soil	
3.60	916	76.0
4.50	806	28.5
5.30	697	5.9
5.95	594	1.4
7.10	251	.1
7.45	297	.05
8.00	303	.01
8.60	251	.003
9.20	200	.0008

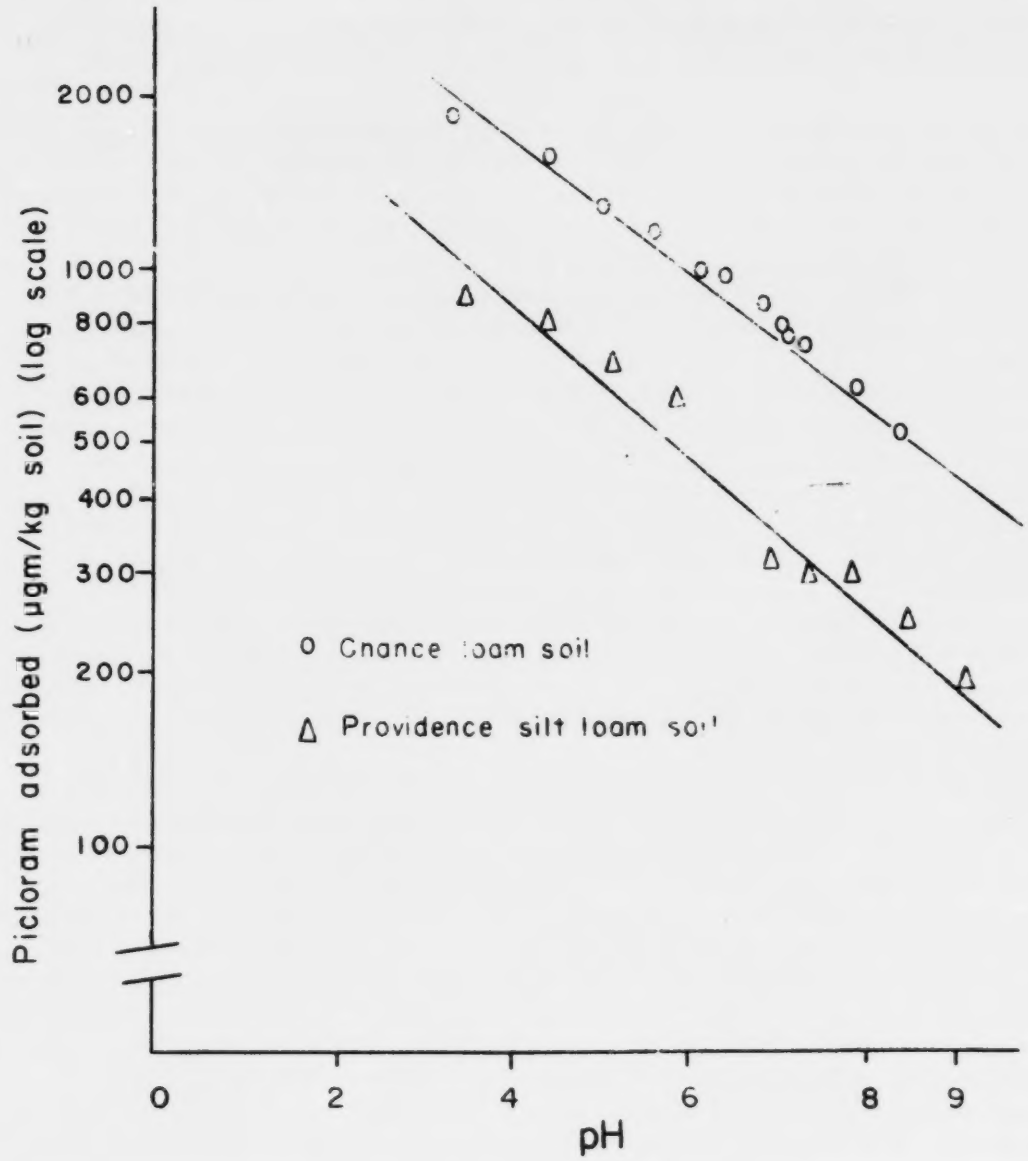

Figure 4. Picloram adsorption by Chance loam and Providence silt loam soils as influenced by the pH of soil suspension.

soil is governed, to a large extent, by the hydrogen ion activity relationships which occur between the solution and solid phase of soil.

Although adsorption of picloram is affected by solution pH, it is evident that ionization of picloram is not the only factor. Even above pH's at which picloram was essentially ionized (Table 13), there was a continued decrease in adsorption with increases in pH.

Bailey, White, and Rothberg (7) have suggested hydrogen bonding to clay minerals as a possible mechanism for picloram adsorption. It appears that the proton involved in hydrogen bonding at lower pH values came from the carboxylic group of picloram. A sharp increase in adsorption with decreased pH parallels the sharp increase in undissociated species of picloram (Table 13). Whether or not protons associated with soil constituents play any part is unclear. However, at pH values where the adsorbate is completely ionized or completely undissociated, adsorption changes with pH. Picloram is completely undissociated below pH 2.1; and completely ionized above pH 6.1. Measurements were not made below pH 3.4 in either of the soils. At lower pH values, other complications occur because of solubilization of clay lattice Fe and Al. However, adsorption of picloram above pH 6.1, when the picloram is 100 percent in ionic form, can be considered.

A number of adsorption mechanisms were discussed by Bailey, White, and Rothberg (7) for the bonding of picloram at pH values higher than 6.1 (pKa + 2). The hydrogen bonding through the amino group, through the carboxylic acid group, or bridging through metal cations (by coordination with water), are likely to be influenced by addition of OH^-. They also concluded that surface acidity of montmorillonite is 3 to 4 pH units lower than the pH of the bulk solution. It is conceivable, then, that with the addition of more hydroxyls, protons from weak hydroxyls on clay mineral edges will continue to react. Consequently, any bonding of picloram anions through these protons will be reduced at pH values that seem to be above the pH range affecting picloram ionization. The replaced protons are incapable of reacting with the carboxylic group of picloram in solution due to its acidity (pKa = 4.1). The same explanation applies to replacement of protons from $-NH_2$ and -OH groups of organic matter and -OH groups of hydroxy oxides in the soil.

The above seems to be the most feasible explanation for the reduced adsorption at pH values above $\simeq$ 6.1. However, the increased adsorption below pH 6 can have an explanation other than the result of

increased hydrogen bonding through carboxyl hydrogen. At pH values below ≈ 5.0, there exists a possibility of releasing lattice Fe^{+3} and Al^{+3} due to hydronium (H_3O^+) ions acting on the clay lattice. The released Fe^{+3} and Al^{+3} ions are capable of complex formation with picloram. Increased adsorption can occur as a result of this complex formation.

In summary, the adsorption of picloram by Providence and Chance soils is negatively but strongly correlated with pH of the soil suspension. The mechanism of adsorption at pH values lower than about 6 (pH < pKa + 2) is probably by hydrogen bonding. The hydrogen atom on the carboxylic group would be the most likely part of picloram to be involved in such a bond. Another possibility at much lower pH values (pH < ≈ 5) is the complexation with Fe^{+3} and Al^{+3}, which would be released as a result of hydronium ion attack on the clay lattice. The adsorption mechanism at higher pH values (pH > pKa + 2) appears to be hydrogen bonding through carbonyl group of picloram to the weakly acidic protons on the various functional groups on the organic matter and clays of the soil. Bailey, White, and Rothberg (7) referred to physical adsorption as another possible mechanism at pH > pKa + 2. The above investigators also indicated the possibility of metal-cation-picloram complex directly, or through coordination with water, at pH > pKa + 2.

Adsorption of picloram by Providence silt loam soil (3.52% organic matter) and Chance loam soil (18.7% organic matter) was highly and negatively dependent on pH changes induced by KOH and KCl. This was true even at pH values at which picloram molecules would theoretically be 100% dissociated. Adsorption of picloram by these two soils, and by the additional three soils of diverse properties, was greatly increased by increasing concentrations of $BaCl_2$, KCl, K_2SO_4, $CaCl_2$ and $MgCl_2$ from 0 to 500 meq/l. A complex formation between picloram and metal cations is suggested as a possible mechanism for the increased adsorption.

Hamaker et al. (24) have demonstrated that only one dissociation constant is obtained corresponding to the dissociation of one proton from the carboxylic group of picloram. Accordingly, based on a pKa of 4.1 reported by these authors for the above dissociation, the proportion of the two species obtainable at the pH's of concern in these studies is given in Table 13. It is seen from this table that more than 97% of picloram existed as the anion in these studies.

In preliminary studies on the adsorption of picloram by soils, small amounts of inorganic salts increased picloram adsorption considerably. Due to differences in the water quality used for irrigation, differences in salt content of soils and water, and variations in salt concentrations as the moisture is depleted from soils, the effect of these inorganic salts on picloram adsorption is of interest. No literature, in this respect, has appeared concerning picloram.

Picloram adsorption from 1.0 ppm initial picloram concentration by Providence silt loam soil is given in Table 14. The salts investigated were $BaCl_2$, KCl, K_2SO_4, $CaCl_2$, and $MgCl_2$. Concentration of each electrolyte was 5 meq/l of solution, except $BaCl_2$ and KCl also had concentrations up to 666.0 meq/l and 130.43 meq/l, respectively.

There was, generally, a drop in soil suspension pH with the addition of salts. However, the enhanced picloram adsorption could not be accounted for by the theoretical increase in molecular picloram as a result of drop in pH. Miller (46) has observed significant adsorption changes as a direct effect of pH change occurring within $\pm$ 3 pH units of the pKa value of the various phenols or 2, 4-D sorbed to an organoclay. The pH changes below pH 7 would be within this range since the pKa of picloram is about 4.1. Perhaps the apparent salt effect is largely a pH effect.

The drop in pH was expected on the basis of replacement of exchangeable H^+ from the exchange complex of soil by the metallic cations. However, at higher $BaCl_2$ and KCl concentrations, replacement of protons from the weak hydroxyls of exposed layers of clay minerals, hydroxy oxides, and organic matter $-NH_2$ and -OH groups is also a possibility. An unexplainable slight increase in pH was obtained with the addition of small amounts of $BaCl_2$. Increased salt concentrations induced some increases in picloram adsorption independent of changes in pH; therefore, the pH effect is not likely to be the sole cause of increased adsorption.

The disappearance of picloram from solution with the addition of inorganic electrolytes may have been a result of herbicide precipitation rather than soil adsorption. Such precipitation commonly occurs where salts are added to an aqueous solution containing neutral organic molecules (1). Picloram precipitation was investigated by centrifuging solutions of picloram-$BaCl_2$, and picloram-$CaCl_2$ concentrations from

Table 14. Influence of various salts on the adsorption of picloram by Providence silt loam soil. Initial picloram concentration was 1.0 ppm and incubation temperature was 25° C.

Salt	Salt concentration meq/l	Equilibrium pH	Adsorption µgm/kg soil
$BaCl_2$	0	7.10	356
	1.16	7.40	356
	2.84	7.30	402
	5.53	7.15	442
	62.10	6.41	643
	666.00	5.90	752
KCl	0	7.05	352
	5.0	6.95	388
	74.10	6.66	531
	130.43	6.45	555
K_2SO_4	0	7.05	352
	5.0	6.94	344
$CaCl_2$	0	7.05	352
	5.0	6.79	411
$MgCl_2$	0	7.05	352
	5.0	6.81	387

LSD (.05) = 13.6

5.0 to 500 meq/l. Picloram concentrations before and after centrifuging were not significantly different, indicating that precipitation did not occur.

Comparison of picloram adsorption (Table 14) at 5.0 meq/l of KCl, $CaCl_2$, and $MgCl_2$ revealed that divalent cations, generally, were more effective in increasing adsorption on Providence soil than are monovalent cations. Although the replaced protons did not react with

picloram anion in solution to produce the molecular form at the pH's obtained at 5.0 meq/l concentrations, the divalent ions generally produced a lower pH than did monovalent ions. The increase in picloram adsorption at higher salt concentrations could not be accounted for by theoretical increases in molecular picloram, but the metal cations may serve as a bond between the exchange site and the herbicide. This was suggested by Mortland (48) for organic molecules and clay minerals, and by Hance (26) for linuron adsorbed to several adsorbents saturated with metal cations. Hance (26) concluded that atrazine did not complex this way.

The carboxyl of picloram is the most likely group to be involved in complex formation with the metal cations. However, Providence soil is 74 percent base-saturated in the natural state, and about 85 percent of these bases are the divalent cations, Ca and Mg (Table 15). Therefore, the continued increase in picloram adsorption with increasing $BaCl_2$ and KCl concentrations cannot be the result of picloram complexing with additional Ba^{+2} (or K^+) ions adsorbed on the soil. The picloram adsorption occurring at 130.43 meq/l KCl and 666.0 meq/l $BaCl_2$ concentrations (Table 14) was much higher than expected on this basis.

Table 15. Cationic composition of the exchange complex of various soils.

Soil	Cation exchange capacity	Base saturation[a]	Ca + Mg
	meq/100 gm soil	%	% of exchangeable bases[a]
Nibley silty clay loam	25.7	≈ 100	91.2
Millville silt loam	15.6	≈ 100	83.7
Chance loam	37.0	95.7	87.6
Aiken clay	16.3	49.9	87.1
Providence silt loam	30.5	74.0	84.8

[a]bases denote Na + K + Ca + Mg

It is conceivable that the picloram anion in solution will undergo the following reactions with added metal cations in solution:

$$M^{+2} + P^- \rightleftharpoons \underset{I}{[MP]^+} \overset{P^-}{\rightleftharpoons} \underset{II}{[MP_2]^o}$$

$$M^+ + P^- \rightleftharpoons \underset{III}{[MP]^o} \qquad [1]$$

$$[MP_2]^o + M^{+2} + P^- \rightleftharpoons \underset{I}{[MP]^+} + \underset{II}{[MP_2]^o}$$

where P^- is picloram anion, M is a metal cation, and I, II, and III refer to molecular or ionic species. The most likely constituent of picloram to be involved in the formation of species I and II would be the carboxyl group (7).

The species $[MP]^+$ may be involved in cation exchange with inorganic cations on the exchange complex of the soil. This possibility was suggested by Dekking (15) for the adsorption of polystyrene by kaolinite and montmorillonite. A quantitative estimate of the extent of $[MP]^+$ as a function of M^{+2} concentration in solution is not available, although it would increase with increasing M^{+2} ions.

A number of other possibilities exist for the increased picloram adsorption with enhanced salt concentrations. Salts would change the thickness of the double layer of ions, which could result in increased metal ion-picloram complexation. Hemi-salt formation, which occurs when the amount of adsorbed base on a surface exceeds the number of protons available for cation formation, is also possible. According to Mortland (48), in hemi-salt formation, the already protonated molecule at the surface of clay retains its proton against attraction by the non-protonated molecule, and a cation of $[B_2 - H]^+$ type results. It is possible that additional salts contribute to $[B_2 - H]^+$ formation by making more base (picloram anions) available for bonding. The exact mechanism by which this occurs is not clear.

The increase in picloram adsorption with increasing monovalent cations (K^+, for example, in Table 14) is unexplained. However, from

Equation [1], the species $[MP]^{o}$, the result of monovalent cation and picloram anion interaction, is neutral. It is conceivable that a neutral species will have a greater tendency to adsorb by physical forces (7) than an anionic species, which will be repelled by the negative charges on the soil. McCall et al. (39) found that picloram was adsorbed by cationic resin (H-form), non-ionic resin and anionic resin, respectively. They concluded that picloram was adsorbed mainly in the anionic form by Coulombic forces (electrostatic) and to a lesser degree by weak physical bonding (van der Waal's forces).

The effect of temperature (17.7, 25.0, 28.2, and 34.7° C) on the adsorption of picloram by the Chance loam, Providence silt loam, and Aiken clay soils is given in Table 16. An increase in temperature from 17.7 to 25.0° C resulted in an increase in adsorption. A decrease in adsorption occurred as the temperature increased to 28.2° C and 34.7°C. This suggested that two mechanisms are operative in adsorption.

Table 16. Effect of temperature on the equilibrium adsorption of picloram by Providence silt loam, Chance loam, and Aiken clay soils from 1.0 ppm concentration.

Soil	Temperature °C	Adsorption µgm/kg soil
Providence silt loam	17.7	339
	25.0	371
	28.2	412
	34.7	313
Chance loam	17.7	968
	25.0	1042
	28.2	1020
	34.7	1006
Aiken clay	17.7	268
	25.0	-
	34.7	254

Haque et al. (29) found little effect of temperature on adsorption of 2, 4-D on clays at 25 and 40° C, whereas Talbert and Fletchall (51) found a decrease in adsorption with increased temperatures for simazine-^{14}C and atrazine-^{14}C by Marshall silty clay loam.

Apparently, the two mechanisms of adsorption of picloram, which have opposite temperature coefficients, increase or decrease adsorption depending on temperatures. In earlier studies, Hamaker, Goring, and Youngson (24) reported that diffusion of picloram was a dominant factor in adsorption. Diffusion is an endothermic process, and is enhanced by increases in temperature. An apparent decrease, after an initial increase in adsorption suggests physical adsorption, or a weak bonding, at the pH levels of these soils.

The amount of picloram adsorbed at various herbicide concentrations by Providence silt loam and Chance loam soils is shown in Figure 5 and Table 17. Table 17 shows adsorption values of Aiken soils at two herbicide concentrations. As picloram concentrations in solution were increased from 0.05 to 10 ppm, the amount adsorbed increased (Table 17).

As shown in Figure 6, the adsorption data follow the Freundlich equation (correlation coefficient 0.999). The values of b and n are the y intercept and slope. They were found to be 538.3 μgm/kg and 0.972 for Providence silt loam and 2009 μgm/kg and 0.837 for the Chance loam soil. The value of b can be interpreted to be equal to the concentration of picloram adsorbed by the adsorbent in equilibrium with a unit concentration of the herbicide (in this case 1 ppm).

To study the release of picloram with additional elutions of water, 1 ppm solutions of picloram were allowed to equilibrate with soil at 25° C; the soil:solution ratio was 1:1. The bulk solution, which was in equilibrium with the adsorbed picloram, was diluted with deionized water to create different concentration gradients. The system was then allowed to reach equilibrium. The results are presented in Table 18 for the Providence silt loam soil. Dilutions of equilibrated bulk solution from 1.5 times to 3.22 times the original quantity of water was used.

The data show the amount of picloram remaining after the first wash, the equilibrium concentration of the bulk solution and the theoretical amount of picloram expected to be adsorbed at the three equilibrium concentrations as extrapolated from the adsorption isotherm (Figure 5).

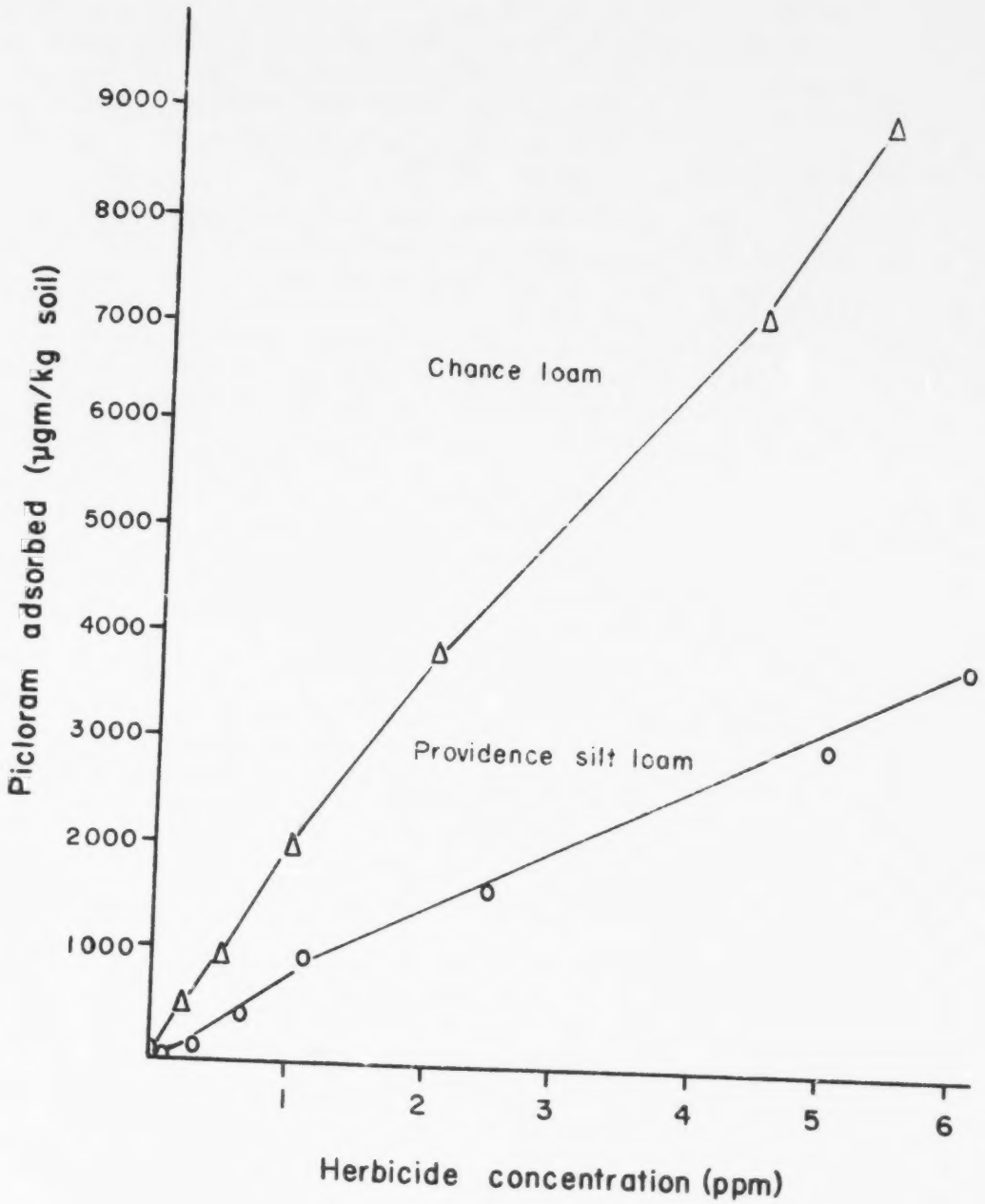

Figure 5. Effect of concentration of picloram in solution on its adsorption by two soils. Adsorption determined at 25° C.

Table 17. Effect of picloram concentration on its adsorption by Providence, Chance, and Aiken soils at 25° C.

Soil	Initial concentration ppm	Equilibrium concentration ppm	Amount adsorbed µgm/kg soil
Providence silt loam	.05	.032	18.6
	.10	.064	36.3
	.50	.325	175.0
	1.00	.652	347.7
	2.015	1.168	863.0
	4.033	2.524	1515.0
	8.0	5.184	2790.0
	10.0	6.436	3611.0
Chance loam	0.5	.209	582
	1.0	.479	1042
	2.016	1.0502	1930
	4.033	2.13	3806
	8.0	4.435	7130
	10.0	5.6134	8773
Aiken clay	0.5	0.433	135
	1.0	0.867	268

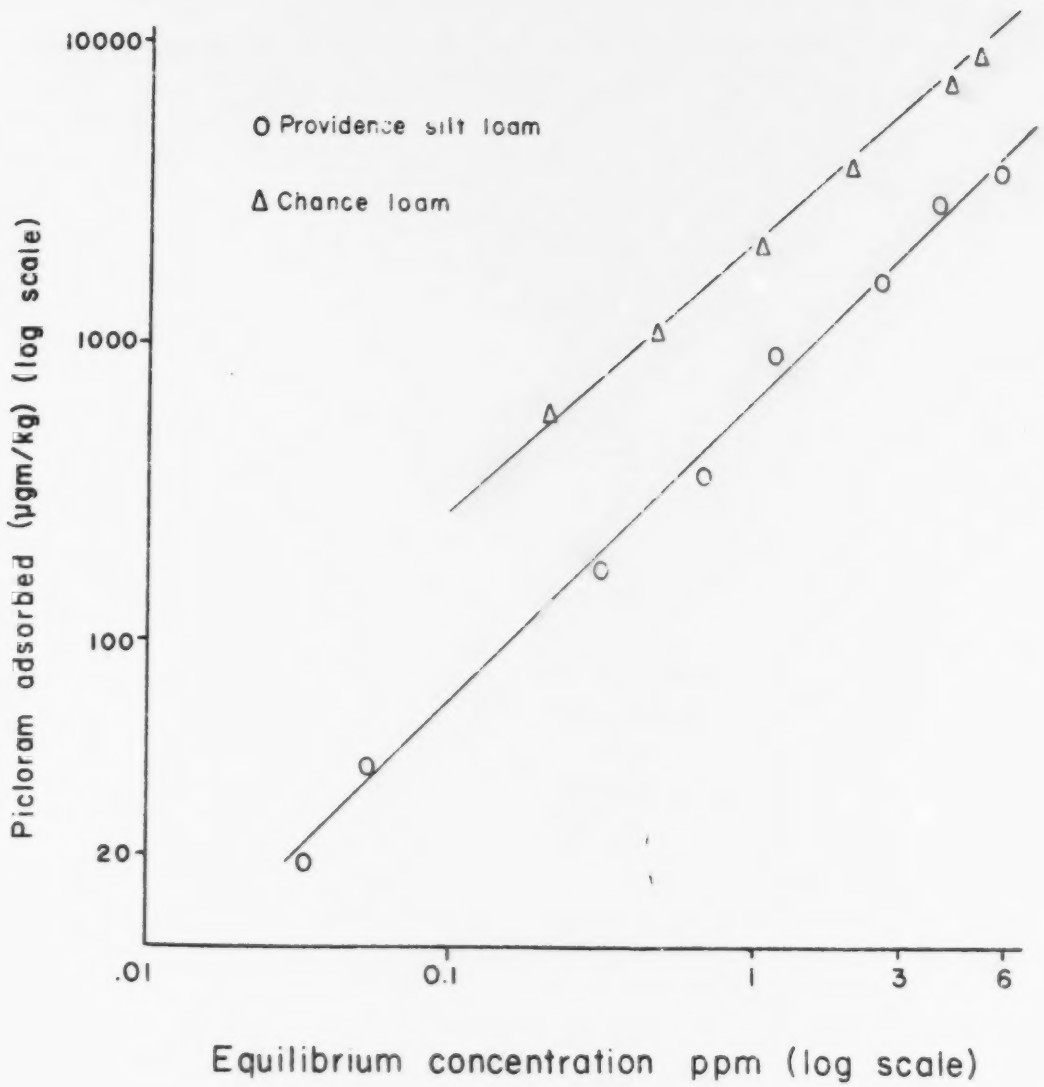

Figure 6. Freundlich plot for adsorption of picloram by Providence silt loam and Chance loam soils at 25° C.

Table 18. Effect of increasing dilution with deionized water on the release of picloram from Providence silt loam soil at 25° C.

Dilution	Picloram desorbed	Equilibrium concentration	Picloram remaining adsorbed after desorption period	Theoretical amount expected to remain adsorbed[a]
	µgm/kg soil	ppm	µgm/kg soil	µgm/kg soil
1.5	96.4	0.480	262	260
2.11	142.5	0.390	229	217
3.22	193.4	0.271	177	150

[a]Extrapolated from the adsorption isotherm

The reversibility of adsorption at lower dilution (1.5) is evident. However, at higher dilutions, the adsorption is not completely reversible. The effect of the soil: solution ratio was studied by an experiment (Table 19) in which soil:solution ratios ranging from 1:5 to 1:0.5 were used. It was found that soil:solution ratios between 1:5 and 1:2.5 did not have any measurable influence on adsorption per unit weight of soil.

Table 19. Effect of soil:solution ratio on the equilibrium adsorption of picloram by Providence silt loam soil from aqueous solutions of 1 ppm concentration.

Soil:solution ratio	Amount of picloram adsorbed μgm/kg soil
1:5.0	345
1:2.5	338
1:1.66	316
1:1.25	350
1:1.00	342
1:0.66	307
1:0.50	268

In an attempt to relate the soil characteristics affecting adsorption of picloram, correlation coefficients were determined (Table 20). Adsorption of picloram was most closely related to organic matter content, pH and sesquioxides (Fe and Al oxides).

Correlation between adsorption and cation exchange capacity was significant at the 0.05 level. Correlation was very poor with clay and silt content. Cation exchange capacity and organic matter are closely associated with each other (Table 21). The pH was negatively correlated with adsorption.

The positive correlation of organic matter with sorption is consistent with the results of Sheets, Crafts, and Drever (54) who reported that organic matter was the best single predictor of herbicide sorption among the four factors of organic matter, clay content, soil pH, and cation exchange capacity.

Table 20. Correlation coefficients (r) between soil properties and adsorption of picloram by five soils.

Soil property	Correlation coefficient[b]
Organic matter[a]	0.99
Cation exchange capacity	0.84
Sand	0.64
Silt	-0.10
Clay	-0.25
Sesquioxides (Fe_2O_3, Al_2O_3)	+0.96
pH	-0.98
Reduction in organic matter[a]	0.98

[a] Chance and Aiken soils excluded

[b] A correlation coefficient of 0.80 at 5 percent level and 0.90 at 1 percent level is required for significance

The role of hydrated Fe and Al oxides as sorption agents was illustrated by the work of Hamaker, Goring, and Youngson (24), who found that organic matter and hydrated metal oxides are principally responsible for the adsorption of picloram on the 10 soils they studied. They found the percentage of sorption of ^{14}C-labelled picloram to be 21 percent and 34 percent in one hour from 1 ppm solution of Fe_2O_3 (amorphous) and Fe_2O_3 (partially crystalline), respectively.

Table 21. Correlation coefficients[a] (r) of various soil properties among themselves.

Soil property	CEC	Sand	Silt	Clay	R_2O_3[b]	pH
O. M.	.18	.52	.1	-.36	-.40	-.48
C. E. C.		.45	.15	-.34	-.54	-.32
Sand			-.49	-.38	.12	-.74
Silt				-.59	-.90	.83
Clay					.74	-.30
Sesquioxides						-.56

[a] A correlation coefficient of 0.81 at .05 level and 0.92 at .01 level is required for significance

[b] Sesquioxides

Factors Affecting Soil Adsorption-Desorption of Picloram (Column Studies)

Columns simulate the field conditions more closely than batch studies, and allow better control of variables. The influence of herbicide dosage level and Ca-saturation of the soil were studied in the two soils, Millville silt loam and Aiken clay. The columns were also used to test the predictability of a mathematical model based on the chromatographic theory of herbicide movement, a theory often used to predict behavior of herbicides in the soil.

Millville Silt Loam Soil

Characteristic properties of this soil are given in Table 1. Since small amounts (5 ml and 3.52 ml) of herbicide solution were used, it was considered necessary to evaluate the possibility of the diffusion of the "penetrated" part of the herbicide into the water on the surface of the soil (back diffusion). A 1.0 ppm solution of picloram was eluted through an 8.9 cm column of Millville soil. The volume of solution

varied from 3.52 ml in one case to 5.0 ml in another. It is seen in Figure 7 that back diffusion effects, expected to be exhibited as hold back (displacing or spreading the distribution curve) are essentially absent. The left side (adsorption phase) of 5.0 ml sample curve is shifted to the left of that of 3.52 ml sample probably because of slightly higher pore water flow velocity of the 5.0 ml sample.

Effect of Application Rate of Picloram. The distribution of picloram eluted from an 8.9 cm column of Millville silt loam soil at two concentrations of picloram is shown in Figure 8. The two curves are essentially identical, except for a slightly higher peak and slightly higher C/C_o points on the desorption side of the elution curve, for the 1.0 lb/A (10.0 ppm). The slightly lower flow velocity (v_o) for the 1.0 lb/A dosage resulted in a greater peak height than expected compared to the lower dosage. However, these differences are assumed to have occurred because of errors of detection, sampling, etc. Figure 8, therefore, shows that adsorption isotherm of picloram on Millville silt loam soil is essentially linear at room temperature from 1.0 ppm (0.1 lb/A) to 10.0 ppm (1.0 lb/A) picloram concentrations.

The appearance of picloram in the effluent (at 0.5 pore volume) much before one pore volume of liquid at both concentrations of picloram indicates molecular diffusion is significant during picloram movement in this soil. One limitation to mathematical prediction of solute movement in porous media, is the inability to adequately characterize diffusion. Nielsen and Biggar (51) have reported that hydrodynamic dispersion increases as v_o decreases; therefore, the diffusion effects noted in this experiment may be related to the v_o's used in these studies.

Effect of Calcium Saturation of the Soil. In Figure 9, the movement of a 0.1 lb/A dosage picloram as related to calcium saturation of Millville silt loam is given. Calcium saturation of the 8.9 cm column of soil did not appreciably affect the amount of adsorption as shown by the peak heights of the curves. The slightly lower peak for the Ca-saturated soil is consistent with a lower flow velocity of water (0.5882 cm hr^{-1}) for this soil. This is consistent with results from batch studies showing that Ca-saturation did not appreciably affect picloram adsorption by this soil.

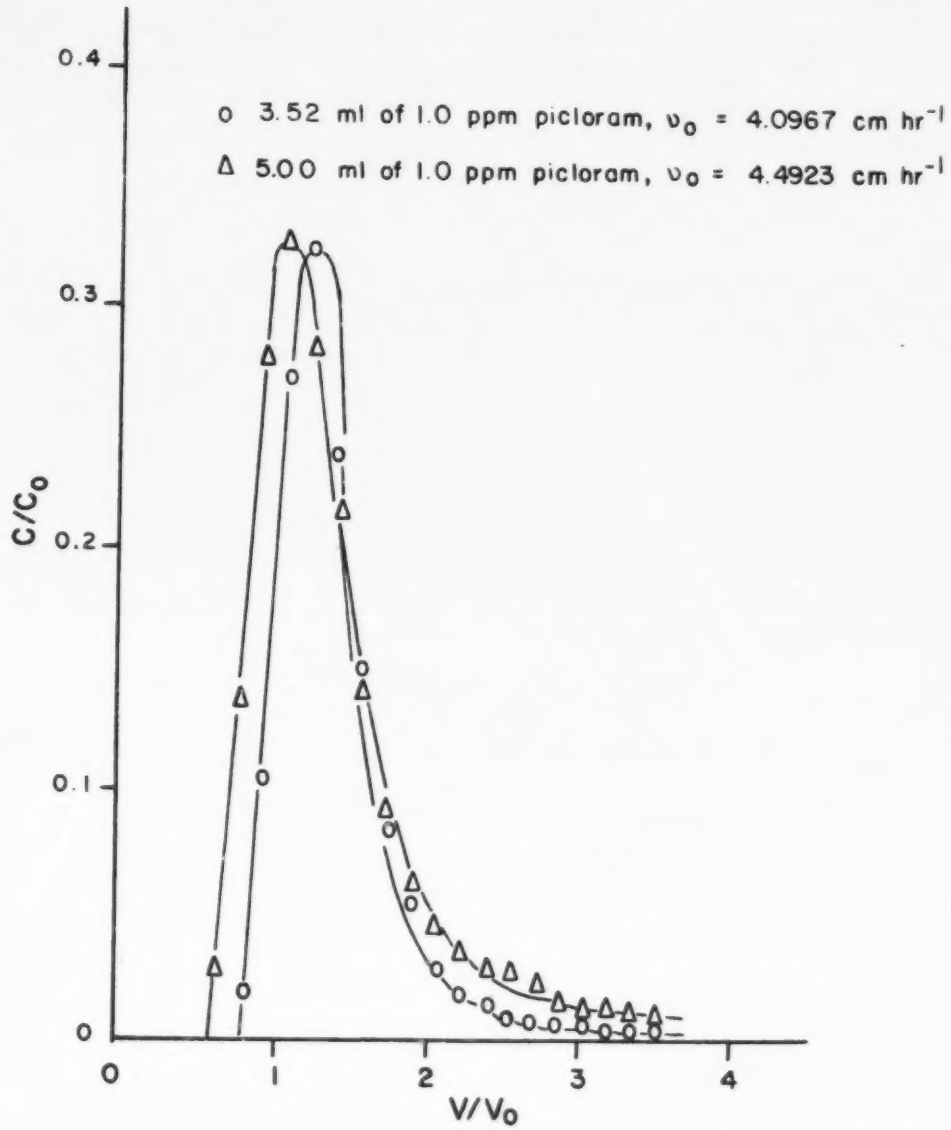

Figure 7. Relative concentration distribution (C/C_o) of picloram in effluent from Millville silt loam soil column as affected by amount of picloram solution added on top of the soil column.

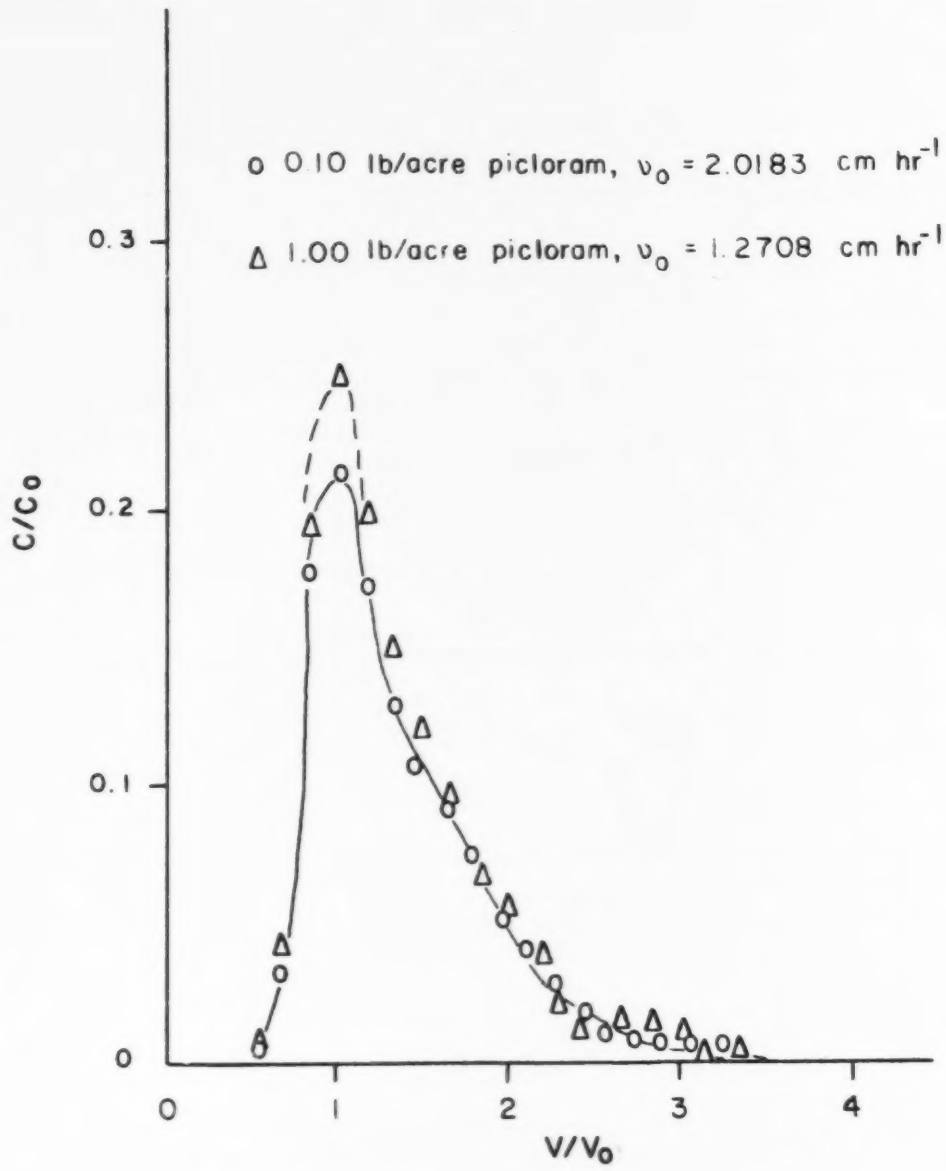

Figure 8. Effect of two rates of picloram application on the relative concentration distribution (C/C_o) of picloram in effluent from Millville silt loam soil column.

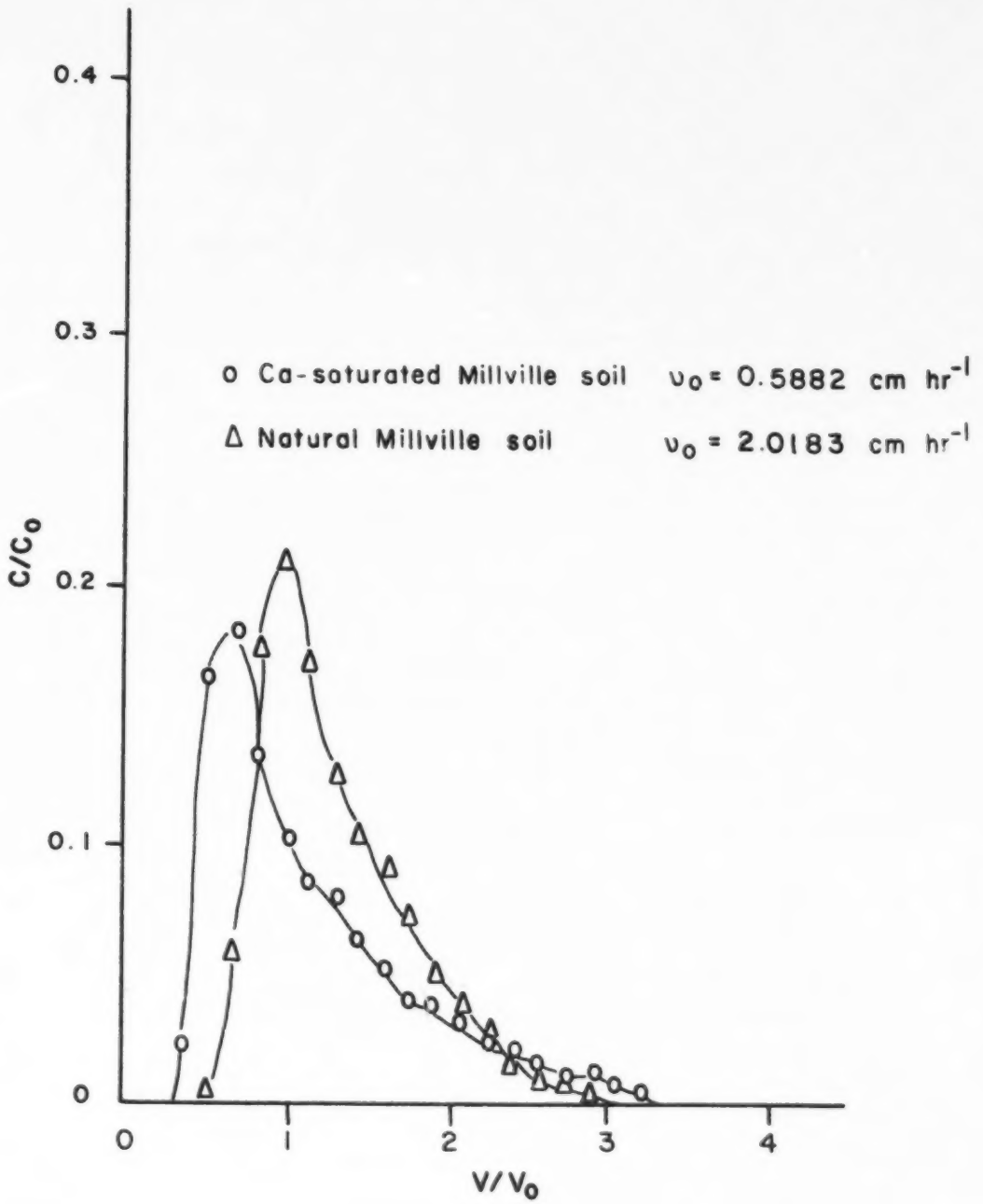

Figure 9. Effect of Ca-saturation on the relative concentration distribution (C/C_o) of picloram in effluent from Millville silt loam soil column.

The flatter desorption leg of Ca-saturated soil (compared to natural soil) indicates slower desorption rate. However, it seems that the effect of pore-water velocity (0.588 vs. 2.02 cm/hr) is superimposed on the effect of Ca^{++} in these data. The relative shape and position of the curves could be rationalized on velocity difference alone.

Aiken Clay Soil

Some properties of the Aiken clay soil are listed in Table 1. Movement of picloram in a soil column (12.3 cm long) was studied as related to herbicide concentration and calcium saturation of the soil.

Effect of Application Rate of Picloram. The distribution curve for 1.0 lb/A dosage is shifted slightly to the right of 0.10 lb/A curve (Figure 10), indicating greater soil adsorption at the higher concentration. The tendency of greater adsorption of the higher dosages is also evident from the later appearance of picloram in the effluent.

Both dosages of picloram started to appear in the effluent of the Aiken soil after about one pore volume of liquid had passed through the column, and all picloram was eluted after 2.25 to 2.5 pore volumes had passed.

Effect of Calcium Saturation of the Soil. Calcium saturation of the Aiken soil increased the herbicide adsorption capacity almost two-fold. The picloram did not appear in the effluent until about 2.25 pore volumes had passed through the salt saturated soil even when the flow velocities were nearly equal. About four pore volumes of displacing liquid were required to elute all of the herbicide. This is consistent with observations from batch adsorption studies with Ca-saturated Aiken soil.

Test of Mathematical Model for Picloram Movement in Natural and Ca-saturated Millville and Aiken Soils

The model of Davidson, Rieck, and Santelmann (13) was used to predict picloram movement in the Millville and Aiken soils. The choice of soils was arbitrary, dictated by their availability. They did, however, represent soils of diverse properties in organic matter,

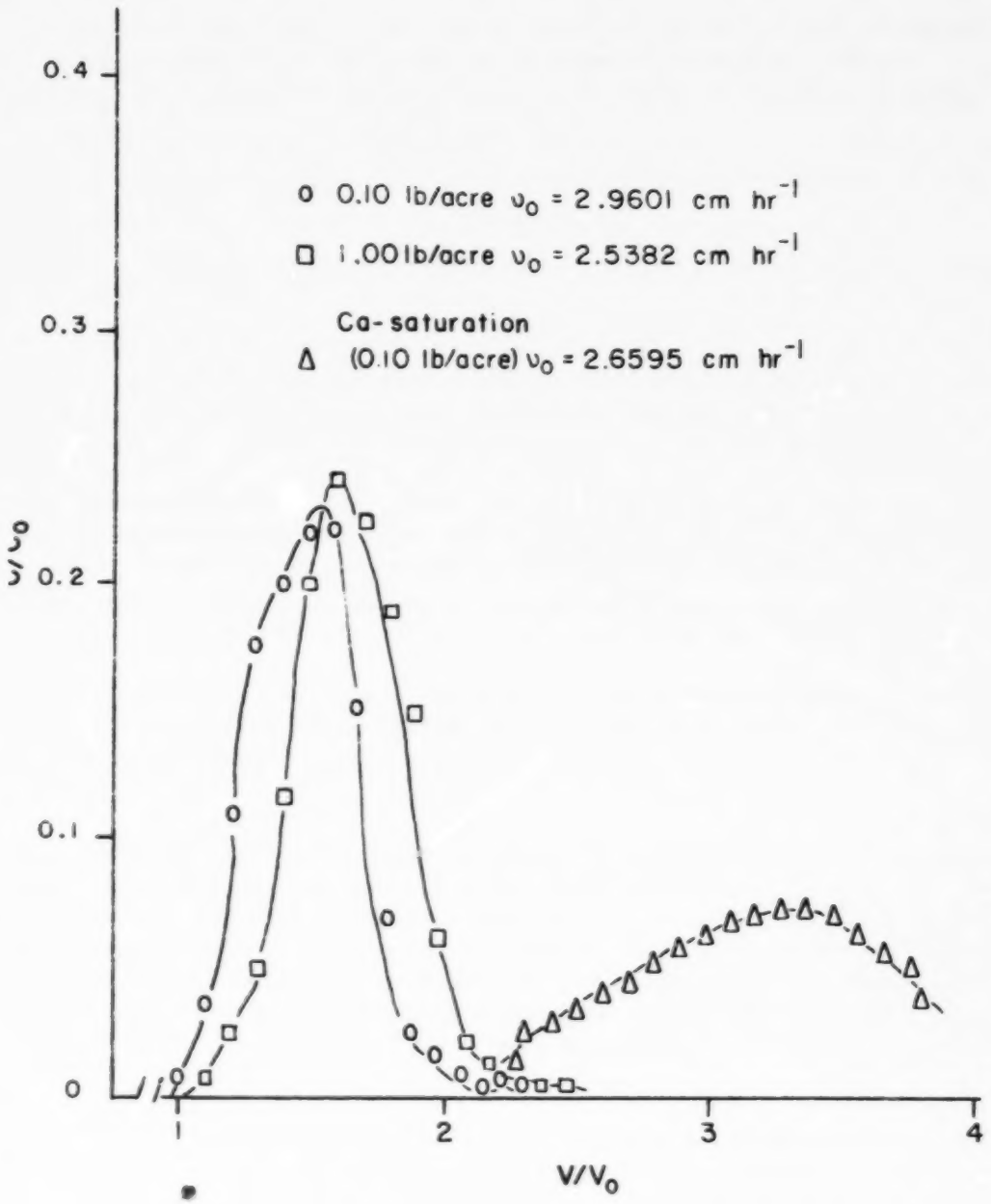

Figure 10. Relative concentration distribution of picloram in Aiken clay soil, (1) as a function of two application rates (2) as affected by Ca-saturation of the soil.

clay and sesquioxides contents; properties found in batch studies to be important in picloram adsorption (See Table 1).

Millville Silt Loam Soil. The relative concentration distribution (C/C_o) as a function of pore volume (V/V_o), i.e., the number of pore volumes passed through the column, is presented in Figure 11. The theoretical distribution curve (solid line) for the same pore water velocity (ν_o) and distribution coefficient (K) calculated from batch studies (Table 22), is also given. The experimental curve is the same as the one given in Figure 9, with picloram applied at 0.10 lb/A and with a ν_o of 2.0183 cm/hr.

Table 22. Physical data for picloram displacement through Millville silt loam and Aiken clay soils.

Soil	ν_o Average pore water velocity $cm\ hr^{-1}$	K' Retardation factor	K'' Adjusted retardation factor
Millville silt loam	2.0183	1.2289	0.971
Ca-saturated Millville silt loam	0.5882	1.2365	0.696
Aiken clay	2.9601	1.6395	0.926
Ca-saturated Aiken clay	2.6595	3.4649	--

The model (solid line) predicts quite well the concentration of picloram in the effluent at the start of the leaching, near the end of leaching and estimates peak height reasonably well. However, the model overestimates adsorption over most of the leaching process as evidenced by the shift of the theoretical curve to the right. The occurrence of peak height of the theoretical curve at a pore volume greater than

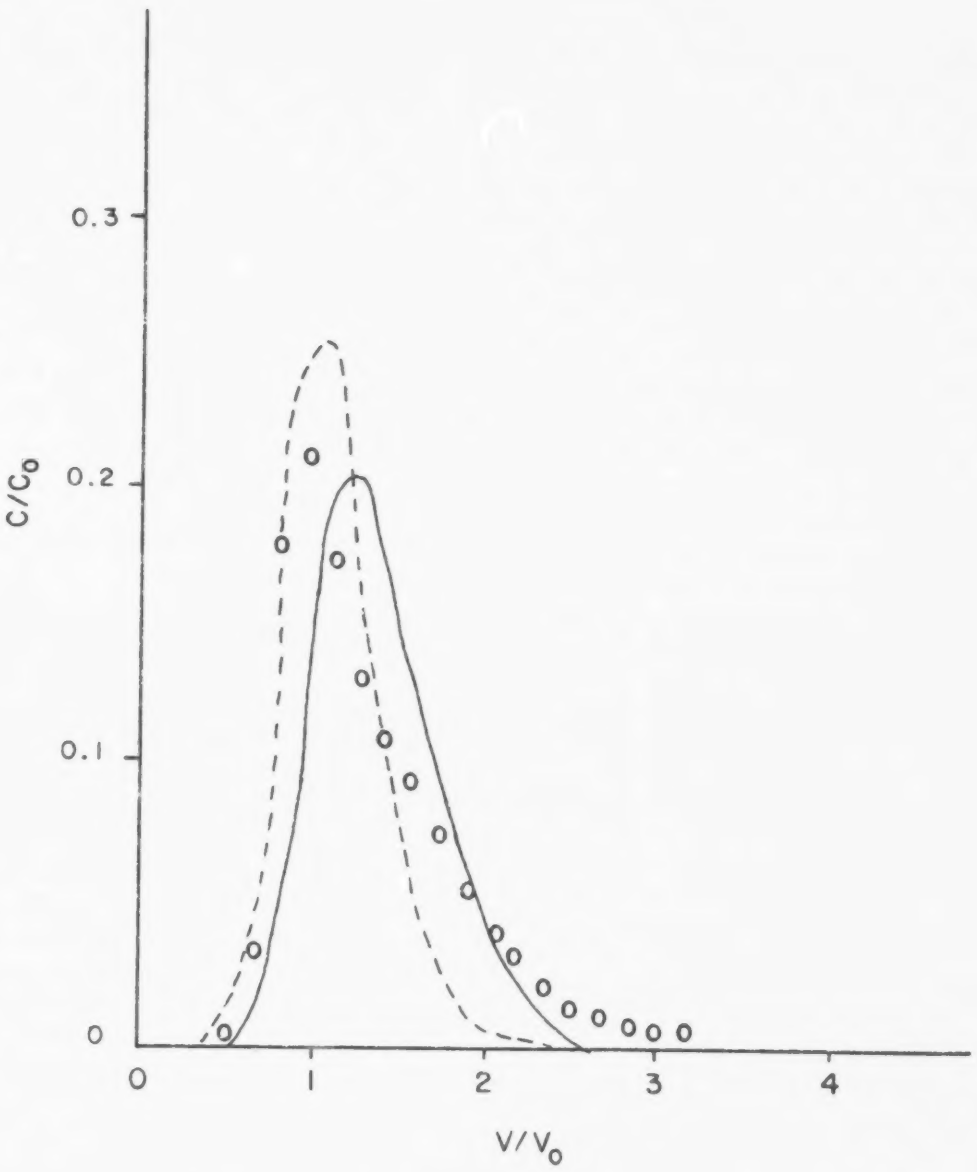

Figure 11. Experimental (o) and calculated relative picloram concentration curve from Millville silt loam soil. Solid curve was calculated from retardation factor (K') from batch studies and dashed curve from 'adjusted factor' (K'') (See Table 22).

was shown experimentally is also indicative of overestimation of adsorption by the model.

Some investigators (9, 12) have encountered similar problems in predicting picloram movement in soils, and have calculated a retardation factor to compensate for the apparent increase in pore volume due to linear retention processes. This factor supposedly helps to correct the overestimation of adsorption. The dashed line in Figure 11 is the theoretical curve based on this lower retardation factor (Table 22). The model adequately describes the left hand (adsorption) side of the elution curve, as well as the position of the peak.

If a lack of equilibrium between the soil and flowing system was responsible for the failure of calculated curves (Figure 11) to describe the movement of the herbicide, then the left hand portion of each distribution curve obtained for different herbicide concentration and column lengths would not be the same (9). The concentration distribution curves for 8.9 and 14.5 cm columns of Millville silt loam soil, at nearly equal v_o's, are shown in Figure 12. The picloram concentration in the effluent for each of the column lengths are similar in the left hand portions of the curve. The lower quantity of picloram recovered from the larger column probably resulted from adsorption of picloram onto the additional soil; the amount of picloram added to each column was the same. The data in Figure 12 show that an equilibrium does exist between the liquid phase and the soil. The amount of picloram adsorbed by Millville silt loam soil in a transient system was less than that determined with the adsorption isotherm procedure (Figure 5).

Ca-saturated Millville Silt Loam Soil. The dotted line in Figure 13 shows the influence of calcium saturation on the movement of picloram through a Millville silt loam soil column. The solid line curve in Figure 13 represents the theoretical curve. The results obtained with the Ca-saturation are similar to those obtained with natural Millville soil (Figure 11). Again, the model overestimated adsorption as indicated by the shift of the theoretical curve to the right of the experimental curve. A lower peak height and slightly more tailing of the theoretical curve on the desorption side was evident. The model was tested using the lower retardation factor and described the data quite well (Figure 13). In order to obtain a fit to the experimental data, the retardation factor used for Ca-saturated Millville soil was 0.696 compared to the value of 0.971 used for natural Millville soil

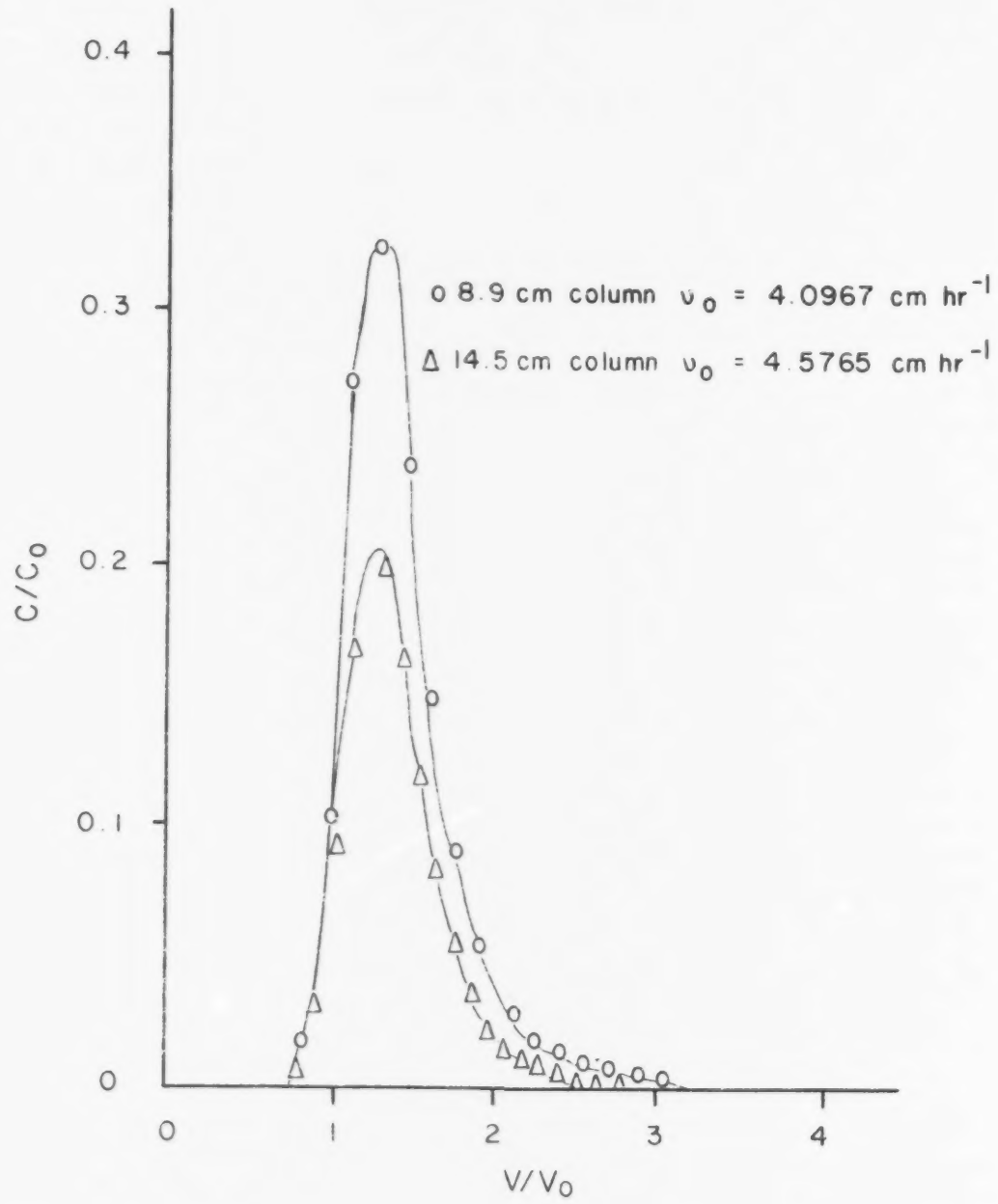

Figure 12. Relative concentration distribution (C/C_o) of picloram in two columns of Millville silt loam soil of different length.

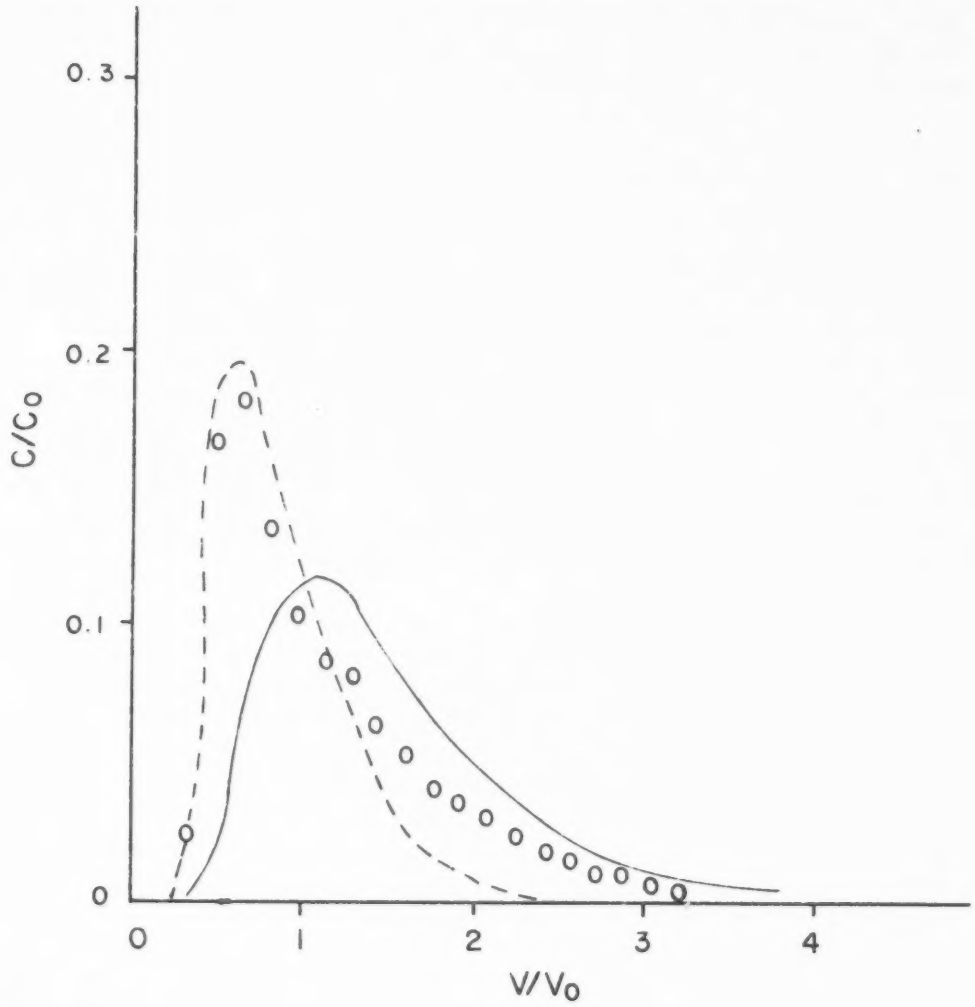

Figure 13. Experimental (o) and calculated relative picloram concentration distributions from an 8.9 cm column of Ca-saturated Millville silt loam soil. Solid curve was calculated from retardation factor (K') from batch studies and dashed curve from 'adjusted factor' (K'') (See Table 22).

(Table 22). Experimental data (Table 22) suggests that the retardation factor for picloram for the Ca-saturated Millville soil should not be very different from natural Millville soil.

Aiken Clay Soil. Figure 14 gives the relative concentration distribution (C/C_o) of picloram in the effluent as a function of pore volumes (V/V_o) of solution passing through columns of Aiken clay and Ca-saturated Aiken clay soil. The solid line (No. 1) in Figure 14 is the theoretical curve for Aiken clay soil based on the retardation factor of picloram obtained from batch adsorption studies (Table 22). Inadequacy of the model to describe the experimental data is evident. The model overestimated adsorption on this soil as shown by the predicted later arrival of picloram in the effluent and the reduced peak height. By selecting a lower retardation factor (dashed curve) for this soil the model described the left hand portion of the curve but was inadequate in some respects.

Ca-saturated Aiken Clay Soil. In Figure 14, the theoretical curve (No. 2) for Ca-saturated Aiken soil is based on the retardation factor of picloram movement in this soil. In this case, however, the model actually underestimated adsorption, as evidenced by shift of the theoretical curve to the left of the experimental points, rather than to the right of the experimental points as obtained in the earlier cases (Figures 11, 12 and 13).

From the discussion above, it appears that part of the failure of the model to describe the movement of picloram in soil columns is related to overestimation of the picloram retardation factor based on the distribution coefficient calculated from batch studies. Although it was established, for the Millville soil (Figure 13), that picloram in liquid flowing through a column was in equilibrium with that in the soil, it seems that the distribution coefficient for picloram changes as the solution moves through the column. When the herbicide first enters the soil column at a concentration C_o, some of it is retained; the solution containing the remaining herbicide moves forward at a lower concentration to be retained and so on, until it travels the complete length of the soil column. This allows a large quantity of herbicide to be retained at the start, but a smaller amount at the effluent end. It offers a possible explanation for the early arrival of picloram observed compared to that calculated using the retention

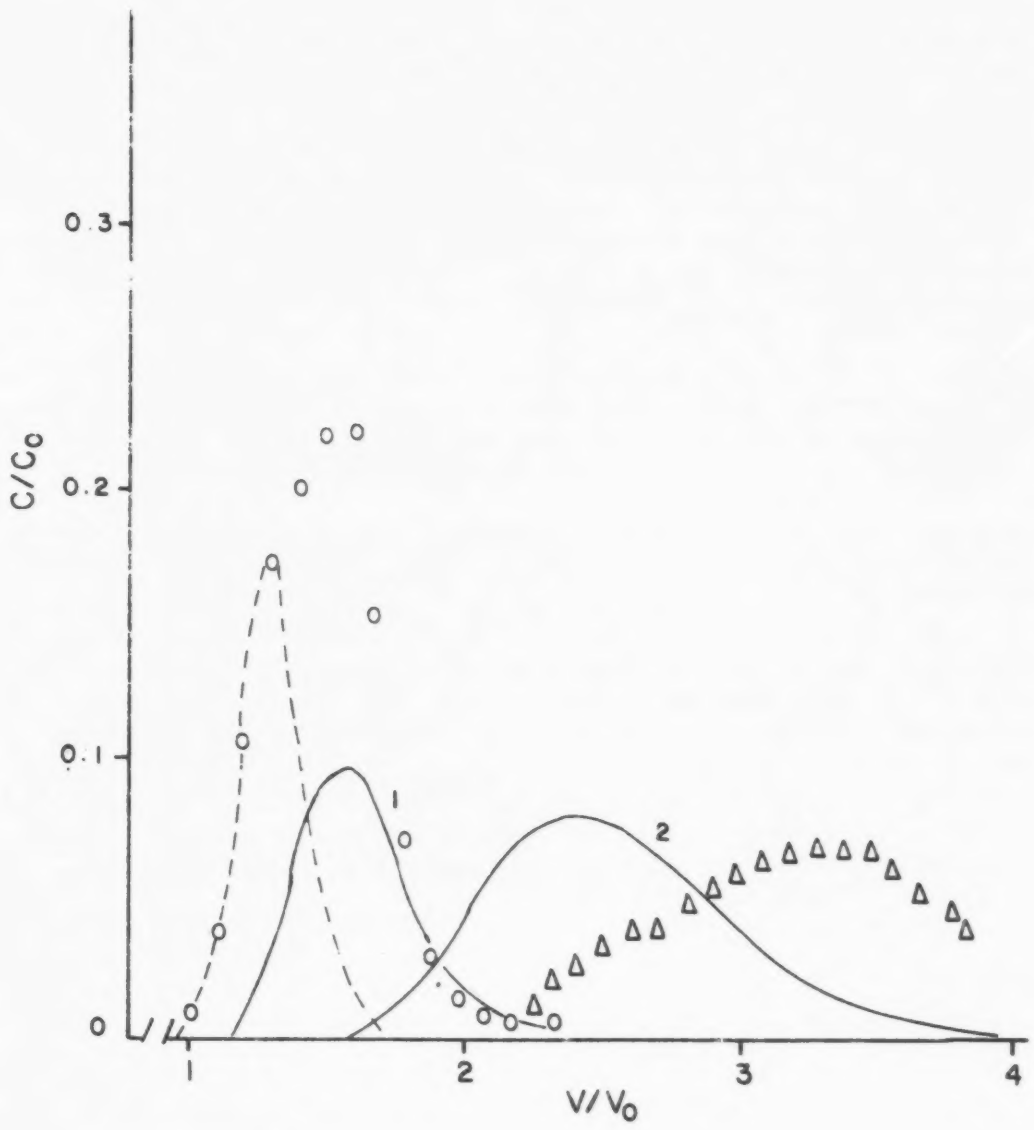

Figure 14. Experimental (data points) and theoretical relative picloram concentration distributions from natural (o), and Ca-saturated (Δ) Aiken clay soil. Solid lines were calculated from retardation factor (K') from batch studies and dashed curve from 'adjusted factor' (K'') (See Table 22).

isotherm. A knowledge of the distribution of adsorbed phase with soil depth would assist in solving this problem.

Few reports were encountered which attempted to determine distributions of adsorbed herbicides at various depths in soil columns undergoing leaching with herbicides. Lai (36) did this type of study with $Ca \rightarrow Mg$, $Na \rightarrow Ca$, and $Na \rightarrow Mg$ exchange in soil columns undergoing miscible displacement with considerable success. Such an approach may be fruitful in the study of herbicides.

A lower retardation factor helped to predict picloram movement for the left hand portion of the distribution curve only. Further studies may benefit from an approach similar to the one used by Lai (36) in which he utilized a gradation of retardation factors as a function of soil depth.

Davidson, Rieck, and Santelmann (13) and Cargill and Davidson (9) studied fluometuron (a urea derivative herbicide) movement and Davidson and Chang (12) studied picloram movement in soil columns and used the model to predict herbicide movement. They reported that the model failed to adequately predict herbicide movement in soil columns and that the prediction was improved by assuming a lower retardation factor. They suggested that mixing processes in the column, a consequence of different size pores, could be a complicating factor in prediction. The distribution of the solute as a function of soil depth may account for differences that result from differential adsorption when a solution moves through varying size pores in the soil at different velocities (mixing).

SECTION VII

SUMMARY

The results of field studies of the lateral movement of herbicides indicate that small but significant amounts of herbicides are transported in irrigation runoff or surface runoff following periods of natural precipitation. The concentration of herbicides in canal water following heavy dosage applications to control ditchbank weeds was detectable in the initial flush of water as the canal was filled with water. The concentration of herbicide in the initial flush of water is quickly diluted to levels below that necessary to cause injury to crops or animals subsequently using the irrigation water. Fall applications of the higher dosages to control persistent ditchbank weeds appeared to be a safe practice if the natural precipitation moved the herbicide into the soil prior to filling the canal with water. Diuron and atrazine were observed to behave similarly when used as ditchbank herbicides; the low concentrations that were observed in the water samples would not likely be hazardous to crops or animals with either herbicide.

Small but significant amounts of GS-14254 are transported in irrigation runoff from a stand of alfalfa established in a clay loam soil. The concentration of GS-14254 in the water decreased rapidly with increased distance from the treated plots and with time.

The movement of picloram, 2,4-D and 2,4,5-T in natural precipitation runoff from range sites was observed when runoff occurred immediately after spraying. The concentration of the herbicides diminished as a function of distance below the treated area and time after herbicide application. Picloram was consistently observed in runoff water collected 100 meters below the treated plots but only one sample collected more than 100 meters below the plots contained detectable amounts of picloram. The tendency for 2,4-D to move in surface water was slightly greater than for picloram or 2,4,5-T but 2,4-D was not observed in measurable amounts when the samples were taken more than 1000 meters from the sprayed areas.

Equilibrium studies on five soils, Chance loam, Providence silt loam, Nibley silty clay loam, Millville silt loam, and Aiken clay, with varying organic matter contents, were conducted to study the influence of various soil variables on the adsorption and desorption of picloram (4-amino-3,5,6-trichloropicolinic acid). Comparison of the adsorption of these soils before and after removal of organic matter (at 350° C)

revealed that up to 91 percent of the adsorption could be accounted for by organic matter.

The five soils adsorbed from 10.8 to 58.2 percent of the added picloram in the picloram concentration range of 0.05 to 10 ppm. At the 0.01 level, adsorption was significantly correlated with organic matter ($r = 0.991$), pH ($r = -0.98$) and sesquioxides content ($r = 0.96$) of the soils and was significantly correlated with CEC ($r = 0.84$) at the 0.05 level. However, CEC and organic matter were also correlated with each other. Correlation between adsorption and clay content of the soils was poor.

Kinetic studies on the five soils revealed that soils with higher amounts of organic matter take longer to reach equilibrium, (up to 120 hours). Studies of the effect of temperatures from 17.7° C to 28.2° C on picloram adsorption by three of the five soils revealed that the picloram adsorption within this temperature range is endothermic. A further increase in temperature to 34.7° C decreased picloram adsorption.

Adsorption by two of the soils, Chance loam and Providence silt loam, was linear at 25° C from 0.05 to 10 ppm initial picloram concentrations.

In studies of the effect of induced pH on picloram adsorption by Chance loam and Providence silt loam soils, it was found that adsorption was inversely related to pH of soil suspension from pH 3.6 to pH 9.2. The regression equations relating the adsorption with pH were:

Chance loam soil:

$$\log_{10} (\mu\text{gms adsorbed/kgm soil}) = 3.654 - 0.107\ \text{pH}$$
$$r = 0.993$$

Providence silt loam soil:

$$\log_{10} (\mu\text{gms adsorbed/kgm soil}) = 3.460 - 0.125\ \text{pH}$$
$$r = 0.985$$

In studies on desorption from the three soils, Providence silt loam, Nibley clay loam, and Millville silt loam, with two successive water extractions, it was shown that 41.0 to 71.8 percent of the initially adsorbed picloram could be desorbed at 25° C with the first two extractions. The desorption thereafter was very slow.

Contrary to reports in the literature concerning precipitation of herbicides with the addition of inorganic electrolytes, no evidence was found of this occurring in picloram solutions without soil. Inorganic electrolytic salts did not appear to significantly alter the adsorption or desorption of picloram on the soils tested; the inorganic salts used were $BaCl_2$, KCl, K_2SO_4, $CaSO_4$, $CaCl_2$ and $MgCl_2$. The divalent cations appeared to be more effective than monovalent cations in increasing picloram adsorption. The results, in this respect, however, were not conclusive. The magnitude of picloram adsorption by Nibley, Millville, and Chance soils was generally the same whether natural soils or Ca-saturated soils were used. These observations suggested an exchange type reaction of picloram with soil, picloram acting as a cation.

Work with Aiken soil, high in hydroxy oxides of Fe and Al and low in bases, provided further evidence that another mechanism for picloram adsorption is through hydrogen bonding. Ca-saturation of this soil resulted in increased picloram adsorption by two-fold, suggesting that cation-complex formation with the soil surface is also a mechanism of picloram adsorption.

Column studies of picloram with Millville and Aiken soils corroborated the observation that picloram adsorption is essentially linear between 1.00 ppm and 10.00 ppm concentration. Ca-saturation of these soils did not appreciably affect picloram movement in Millville soil, but considerably reduced it in Aiken soil. This is in agreement with data obtained in batch studies and showed that batch work is reliable in estimating picloram movement in soils.

Applicability of a mathematical model to picloram movement in soils columns was tested. After adjusting the retardation factor, prediction of picloram concentration in the column effluent improved. However, the prediction was not good after the peak concentration was attained. This was probably due to changing distribution coefficients of picloram with soil depth.

SECTION VIII

ACKNOWLEDGMENTS

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SECTION XI

APPENDICES

A Structure of Some s-Triazine and Phenyl Alkanoic Acid Herbicides Referred to in the Manuscript

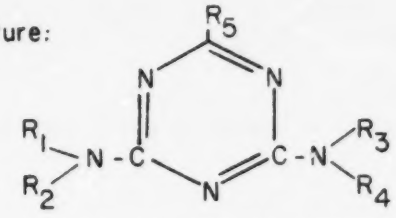
B Cleanup and Extraction Procedure for Picloram in Water Samples

APPENDIX A

Structure of Some s-Triazine and Phenyl Alkanoic Acid Herbicides Referred to in the Manuscript

s-Triazines

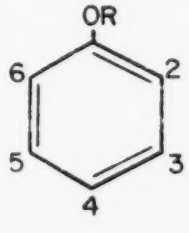
General structure:

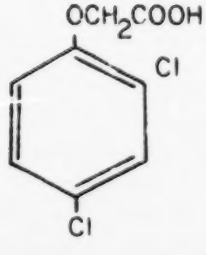


Common Name	Specific Groups				
	R_1	R_2	R_3	R_4	R_5
Atrazine	H	$-CH(CH_3)_2$	H	$-C_2H_5$	Cl
Prometone	H	$-CH(CH_3)_2$	H	$-CH(CH_3)_2$	$-OCH_3$
Simazine	H	$-C_2H_5$	H	$-C_2H_5$	Cl

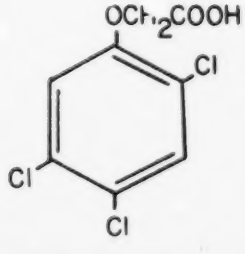
Phenyl Alkanoic Acids

General structure:





2,4-dichlorophenoxyacetic acid



2,4,5-trichlorophenoxyacetic acid

APPENDIX B

Cleanup and Extraction Procedure for Picloram in Water Samples

A procedure for the extraction of picloram from water samples suitable for gas chromatograph has been developed. The water samples from appropriate places along the waterways are collected in dark-colored bottles. The sample-containing bottles are kept in the dark in cold storage. Picloram extraction and determinations are made as soon as possible after the collection of samples.

Extraction

A 500 ml water sample is acidified with HCl immediately after taking it out of the cold storage. The pH of the sample is brought to 2 by adding HCl. The acidified sample is transferred to a separatory funnel and washed with 100 ml of purified diethyl ether. The separatory funnel is shaken for 3-4 minutes so as to thoroughly mix the ether and water. The two layers are allowed to separate for 10-15 minutes. The ether portion is separated from the water with the help of a separatory funnel. Following the first washing, a second 100 ml portion of the diethyl ether is added to the water sample in the separatory funnel. The second portion of the diethyl ether is shaken and after separating from the aqueous layer, is drawn from the separatory funnel. The two ether fractions are combined and the water layer discarded.

Evaporation

The diethyl ether containing picloram is evaporated at 40° C under vacuum in the flash evaporator.

Pyrolysis

After the ether has been completely removed, the picloram is subjected to pyrolysis (Figure 1). The picloram is pyrolyzed between 190 to 200° C, under vacuum to decarboxylated picloram (Figure 2). The decarboxylated picloram is thoroughly washed from the collection flask with double distilled acetone. The sample is then ready for gas chromatographic analysis.

The standards are prepared in the laboratory by the addition of known concentrations of picloram in water. The standard and check samples are extracted in the same manner as field samples. The concentration of picloram in waterways is determined by comparing with the standards.

GLC Procedure

Gas Chromatograph: Varian Aeorgraph Model N. 1800 with electron capture (H^3 or Ni^{63}) detector was used.

A 5-foot glass column containing 5% SE 30 on Gas Chrom 80W. Operating conditions: column 195° C, injection port 205° C, detector 205° C, nitrogen carrier gas 30 ml/min through a nitrogen filter.

Condition column overnight at required temperature. When the column is conditioned, inject 5 λ of each sample into gas chromatograph. If response is too great, dilute solutions.

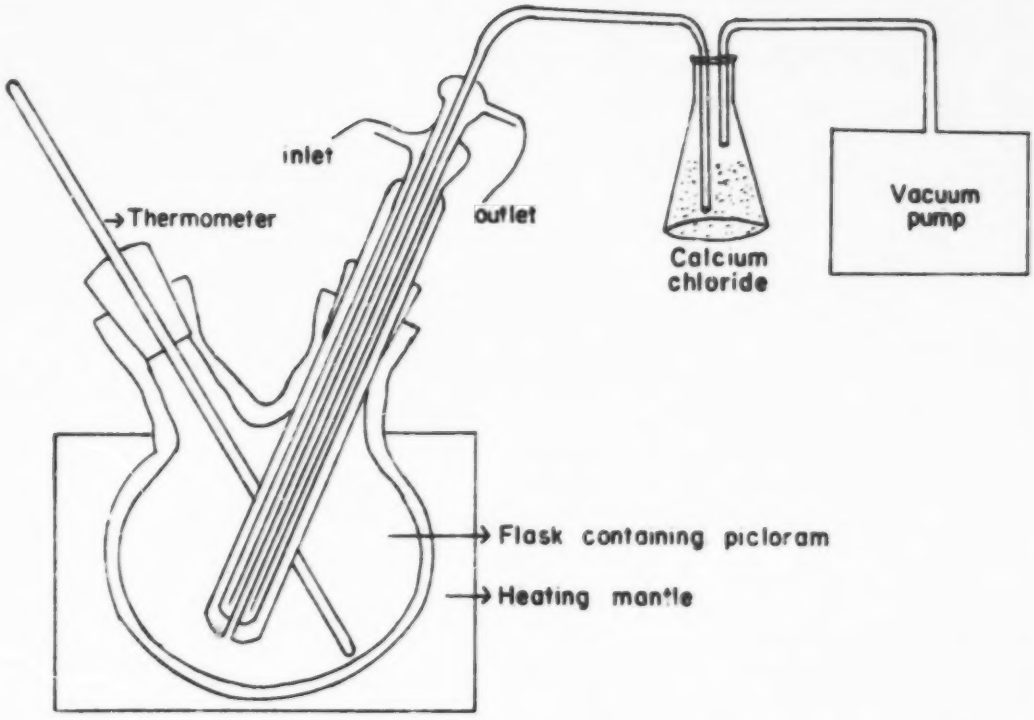


Figure 1. Typical apparatus for pyrolysis of picloram after removal of extraction solvents.

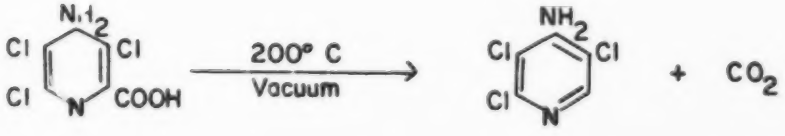


Figure 2. Probable reaction sequence of picloram subjected to thermal pyrolysis.

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